THE EFFECT OF ORTHOPHOSPHATE AS A COPPER CORROSION

INHIBITOR IN HIGH ALKALINITY DRINKING WATER SYSTEMS

THESIS

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Abstract

The purpose of this research was to investigate orthophosphate as a corrosion inhibitor for copper pipe in a high-alkalinity drinking water system. Specifically, this thesis sought to answer three research questions regarding the impact of orthophosphate treatment, the nature of the mechanism by which orthophosphate controls copper corrosion, and the value of equilibrium modeling in predicting orthophosphate's effects. The research questions were answered through a comprehensive literature review and experimental methodology integrating laboratory jar tests, water sampling and analysis from a field investigation, qualitative solids analysis, and equilibrium model application. This study analyzed field data obtained over the course of a year from a high alkalinity water system into which orthophosphate was added to control copper concentrations.

This field research generally supports results previously reported in the literature: in high alkalinity, neutral pH water, a dosage of 3 – 4 mg/L orthophosphate can reduce copper levels in a drinking water system from over 2 mg/L to below the 1.3 mg/L USEPA action level. While surface solid analysis did not provide conclusive evidence confirming the nature of orthophosphate's control mechanisms, jar tests and equilibrium solubility models were demonstrated to provide useful quantitative predictions of how orthophosphate reduces copper concentrations in various waters.

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Stephen Grace

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IN HIGH ALKALINITY DRINKING WATER SYSTEMS

I. Introduction

1.1. Overview

The purpose of this research was to investigate the effect of orthophosphate as a

corrosion inhibitor for copper pipe in a high-alkalinity drinking water distribution system.

While many public utilities currently use orthophosphate treatment to reduce dissolved

copper concentrations in drinking water, the reactions between orthophosphate and

copper pipe are not completely understood. This research was intended to advance

knowledge in the field by observing the effects of orthophosphate on the level of

dissolved copper and by observing changes in the pipe surface. The results of the

research will contribute to the further development of a predictive copper solubility

model, and will provide data that can be reviewed by utilities considering use of

orthophosphate as a corrosion inhibitor.

1.2. Background

Copper metal is a good thermal and electrical conductor. Copper and its alloys

are commonly used in drinking water distribution systems due to their workability and

relatively low solubility. Soluble copper levels in drinking water have implications for

human health: trace amounts of copper are necessary for human enzyme activity and

electron transport, but excessive copper exposure can cause gastrointestinal distress,

liver, or kidney damage (Pontius, 1998). While the adverse effects of dissolved copper in drinking water are not as severe as those of dissolved lead, under the Lead and Copper Rule of 1991, the United States Environmental Protection Agency (USEPA) established an action level of 1.3 mg/L for copper in drinking water systems to reduce potential health effects. In addition to human health concerns, low levels of soluble copper are desired to maintain the drinking water's aesthetics (taste, appearance), reduce discoloration in fixtures, and maintain the strength of the plumbing system. Suppliers have sought to control the dissolved copper levels in drinking water using a number of chemical and physical processes, including pH/alkalinity adjustment, addition of corrosion inhibitors such as orthophosphate, and reduction in stagnation time to minimize contact between the water and copper pipe.

Although copper is insoluble in pure water, copper pipe in contact with the oxidizing agents present in any real drinking water system will experience corrosion until equilibrium is established. Electrochemical reactions will result in the development of an oxide scale at the copper surface and the release of copper ions into solution (Schock et al., 1995). Three general factors contribute to the extent of those reactions and the resultant concentration of dissolved copper in a copper-pipe drinking water system: 1) the water quality parameters (i.e., pH, temperature, alkalinity, dissolved inorganic carbon); 2) the characteristics of the copper pipe itself (i.e., age, chemical composition of the interior surface); and 3) the effect of any engineered corrosion inhibitors used by the water supplier (Edwards et al., 2002).

1.3. Problem Statement

Since the implementation of the Lead and Copper Rule, numerous public utilities have exceeded the 1.3 mg/L soluble copper action level. While violations have occurred throughout the United States, in a variety of geographic locations, and across a range of pH levels and alkalinities, high levels of dissolved copper are particularly common in facilities that are served by utilities that rely on groundwater and that take no corrosion control measures (Schock et al., 1995). An example of such a facility is the Wright-Patterson Air Force Base Child Development Center (WPAFB CDC), where high-alkalinity groundwater is used as the water source. Between 2004-2005, high levels of copper were detected in drinking water samples taken from the WPAFB CDC, in many cases double the 1.3 mg/L action level (Shaw, 2005). To address the problem, WPAFB contracted for the installation of a chemical feed system to add orthophosphate solution to the drinking water at the facility's main water service line. This approach was based on USEPA's research indicating that orthophosphate would create a protective film barrier between the copper pipe surface and the water, thus reducing the levels of copper in solution. Although 56% of surveyed U.S. utilities reported using phosphate inhibitors during 2001, there is little understanding of the nature of the inhibition reactions; industry relies on vendor data, trial-and-error dosing, and anecdotal evidence in their inhibitor selection (McNeill and Edwards, 2002). The USEPA's cupric hydroxide model was developed in an effort to address this deficiency. Extensive laboratory testing was conducted in order that the effect of orthophosphate could be predicted for given water chemistry parameters; however, traditional field studies have produced little data,

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particularly based on solids analysis, that can be used to refine the model's constants (Schock et al., 1995).

1.4. Research Focus

The subject of this study was an investigation of the effect of orthophosphate treatment on copper solubility in drinking water systems by observing the impact of an orthophosphate injection system on copper concentrations over time. This research provided a test case to determine how the USEPA's model correlates to observed field results in a particular environment and will assess the effectiveness of phosphate treatment to reduce copper solubility in a high alkalinity water system. The investigation of orthophosphate treatment in high alkalinity water is of specific interest in areas such as the U.S. Midwest, due to the water's higher buffering capacity and subsequent resistance to pH adjustment (USEPA, 2003).

1.5. Research Objectives/Questions/Hypotheses

The objective of this research was to observe the impact of orthophosphate as a copper corrosion inhibitor in a high alkalinity drinking water system. The hypothesis was that orthophosphate will reduce the level of dissolved copper in drinking water by forming a phosphate scale on the pipe surface, thereby validating the cupric hydroxide model's predictions. Three specific questions were considered:

1. How does the addition of orthophosphate affect copper corrosion in high-alkalinity drinking water systems?

2. What is the nature of the reaction occurring at the copper pipe/water interface after the introduction of orthophosphate to the system?

3. Do observed field measurements of dissolved copper correspond to equilibrium model predictions? If not, what parameters might be the cause of the discrepancy?

1.6. Research Approach

While most prior studies of orthophosphate treatment have focused on water sampling, this research was unique in that it combined both water and solids sampling to provide a more comprehensive analysis of systemic changes. To determine how orthophosphate affects copper corrosion in high-alkalinity water, this investigation measured the levels of dissolved copper in the CDC before and after the installation of an orthophosphate system.   To study the nature of the reaction occurring at the metal/water interface, this investigation considered the results of the water quality analyses along with x-ray diffraction (XRD) and stereomicroscopic analysis of the copper pipe to observe any changes in the surface composition. By performing a series of controlled jar tests and entering the water quality parameters in the EPA's cupric hydroxide model, this investigation compared field results with model-predicted values, and identified those factors which may account for any discrepancies.

1.7. Significance

Field results from the water sampling and solids analyses were compared to the USEPA's cupric hydroxide model to determine the model's applicability to the high-alkalinity field conditions in this experiment. Given the challenges presented in trying to treat these waters, this information is very relevant nationwide. An ancillary benefit of the research is that it provided WPAFB with an assessment of the orthophosphate treatment's effectiveness and whether or not daily flushing of the facility's drinking water

should be discontinued while the orthophosphate system is in operation, along with recommendations about other potential applications of this type of treatment. While supporting several general conclusions about the effectiveness of orthophosphate treatment, one limitation of this research is the fact that all field data was drawn from a single facility.

The research will contribute to overall understanding of the action of orthophosphate on the surface of copper drinking water pipes. It has provided field data to help validate the cupric hydroxide model. It also provides an assessment tool for predicting the level of orthophosphate required to achieve a required reduction of soluble copper, giving water systems engineers with a useful tool to help determine orthophosphate doses.

II. Literature Review

2.1. Copper Characteristics and Use in Potable Water Systems

Copper is a nonferrous metal, atomic number 29, which is distributed on an average of 68 ppm throughout the earth's crust, making it the world's twentieth most abundant element. The element occurs in several valence states; $Cu(I)$ and $Cu(II)$ compounds are the most prevalent, while the other states, $Cu(0)$, $Cu(III)$, and $Cu(IV)$, are rare. While some pure copper metal exists naturally, most industrial copper is produced through an electrochemical reduction of copper ore compounds (Schugar, 2002). The reduction product, $Cu(0)$, is thermodynamically less stable, and tends to oxidize (corrode) in the presence of water (Mattsson, 1989). Copper is an important commercial material due to its high electrical conductivity, low reactivity, and adaptable physical properties (Schugar, 2002). A valued industrial metal, it has been used by humans for over 7,000 years; copper artifacts from the Middle East have been dated to the sixth century B.C. (Schroeder et al., 1966). Copper's appearance as a plumbing material in the U.S. became widespread during the past sixty years; by 1993, the Copper Development Association reported that over 80 percent of all manufactured copper tubing was being installed in plumbing systems (Lane, 1993). In Germany, over 70 percent of domestic drinking water systems were installed as copper lines by 1990 (Becker, 2002). The abundance, cost, and suitability of copper as a construction material for small-diameter drinking water distribution lines ensure that copper will continue to dominate these systems in the near future.

2.2. Human Health Concerns

In the human body, copper is a component of proteins that perform a range of functions, including biosynthesis of connective tissue, terminal electron acceptance for oxygen metabolism, oxygen transport, and electron transfer (Schugar, 2002). It is considered an essential trace element in human nutrition, supporting energy production, iron absorption, and pigmentation (Pontius, 1998). Studies have shown that on average, daily copper intake is 3200 μg. Copper comes from foods such as shellfish, meat, eggs, vegetables, nuts, fruits, fats, and oils (Schroeder et al., 1966). Researchers have mapped out average copper concentrations in various human tissues and have shown that tissue in high-metabolic organs contain the highest copper levels (Schroeder et al., 1966).

Copper piping appears to reduce initial colonization of microorganisms through a combination of algicidal, fungicidal and antibacterial abilities, although the extent and mechanisms of that resistance are not clearly understood (Dietrich et al., 2004). Recent research confirms ancient folk knowledge, suggesting copper storage vessels may provide human health benefits by eliminating harmful bacteria in drinking water (Tandon, 2005).

Although it is an essential trace element for biological processes, excessive levels of copper can be acutely toxic to humans. Research has shown elevated levels of copper in drinking water can result in gastrointestinal distress, including pain, nausea, and vomiting due to irritation of the intestinal lining or alteration of the intestinal microbe population (Pizzaro et al., 2001). Pizarro et al. (2001) also suggest that the severity of gastrointestinal distress is based on the concentration of ionic copper species passing through the stomach, and therefore, soluble or insoluble copper ingested in drinking

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water results in more severe symptoms than copper ingested in food, which binds the copper ions. Based on epidemiological data from 1977-82, the Centers for Disease Control reported that children are most sensitive to excessive copper ingestion, displaying gastrointestinal distress at copper levels of 7.8 mg/L (Pontius, 1998). Individuals who suffer from Wilson's disease are particularly sensitive to copper ingestion (Pizarro et al., 1966). Wilson's disease is a hereditary disorder that reduces the body's ability to transport and eliminate copper; as a result, individuals with the condition exhibit high copper concentrations in their tissues (Pizarro et al., 1966).

The need to prevent excessive copper levels in drinking water was recognized and addressed in the USEPA's 1991 Lead and Copper Rule (LCR). The LCR was established under the 1986 Safe Drinking Water Act to minimize lead and copper levels in all public drinking water systems by establishing action levels, above which corrective measures must be taken to reduce those metals' concentrations (USEPA, 2004). Under the regulation, the action level for copper is exceeded if more than ten percent of the tap water samples measured during a collection period have a copper concentration greater than 1.3 mg/L (USEPA, 2000). Exceedence of the copper action level is not a violation of law, but a trigger for the drinking water provider to perform corrosion control measures in order to reduce the copper concentrations (USEPA, 2004). Although there has been some disagreement about whether 1.3 mg/L is an appropriate action level, the USEPA continues to support that level as a concentration that meets the required trace dietary requirement while avoiding the lowest observable gastrointestinal effect level by a factor of two (Pontius, 1998): the proposed 2006 amendments to the LCR do not recommend any adjustment to the 1.3 mg/L action level (USEPA, 2006).

2.3. Copper Corrosion and Scaling

Soluble copper initially enters into drinking water due to corrosion of the interior pipe surface. Like all metal corrosion, copper pipe corrosion is an oxidation-reduction reaction, driven by the electrochemical potential created on contact between an oxidizing agent, such as dissolved oxygen, and the copper molecules at the pipe surface. The nature of this reaction is well documented elsewhere: the thermodynamic forces governing copper corrosion and its reaction kinetics are widely reported in corrosion textbooks and empirical research literature (Mattsson, 1989; Lane, 1993; Schock et al., 1995). The effects of scale development, water quality, and copper pipe age on corrosion have been the subject of several recent studies designed to determine the impact of solid speciation on copper solubility (Turek, 2006; Cantor et al., 2003; Lagos et al., 2001). Engineers have sought to counter the effects of corrosion through the use of cathodic protection, the addition of corrosion inhibitors, or the application of surface protective coatings (Mattsson, 1989). Focusing specifically on corrosion control for drinking water systems, the USEPA has developed guidelines that recommend pH adjustment, dissolved inorganic carbon (DIC) adjustment, and phosphate addition (USEPA 2003).

2.4. Orthophosphate Treatment for Corrosion Control

Phosphate treatment can be accomplished using polyphosphates, orthophosphates or a blend of the two phosphorous-containing species. Orthophosphate compounds contain a single phosphorous atom bonded to four oxygen atoms, while polyphosphates are chains composed of multiple phosphorous atoms. The polyphosphate chains, which are characterized by the ability to sequester metals in solution, would typically be

employed when the treatment goal is control of metal precipitation. However, these chains, which are created through dehydration synthesis, have a tendency to hydrolyze to orthophosphate in the presence of water, therefore altering their corrosion control mechanism (Cantor et al., 2000). The principle behind the use of orthophosphate as a corrosion inhibitor is the theory that copper will react with orthophosphate to form low-solubility solids, such as cupric phosphate ($Cu_3(PO_4)_2$), on the interior of the pipe, thereby lowering copper concentration in the water (Becker, 2002). In relatively new copper pipes that have not developed a natural, low-solubility scale, the copper-phosphate compounds produced by the addition of orthophosphate will control the maximum copper concentration, as depicted in the following figure by Edwards et al. (2002):
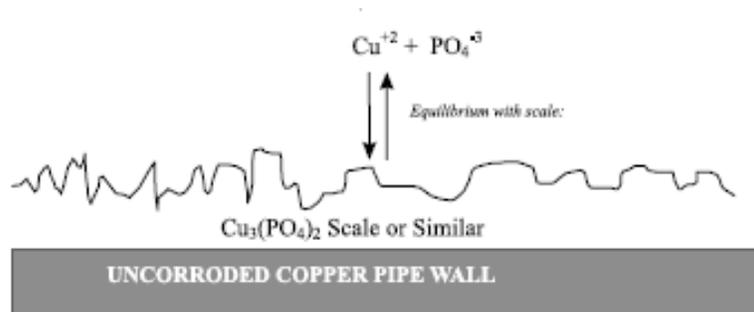
Figure 1. Copper Solubility in the Presence of Phosphate Scale

Schock et al. (1995) illustrate the insolubility of cupric phosphate relative to that of naturally-occurring copper scale (such as cupric hydroxide, $Cu(OH)_2$) by contrasting the solubility constants (K_{sp}) of the two solid species:

Cupric hydroxide: $Cu(OH)_2(s) + 2H^+ \leftrightarrow Cu^{2+} + 2\,H_2O$ $\qquad$ $\log K_{sp} = -19.36$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (Benjamin, 2002)

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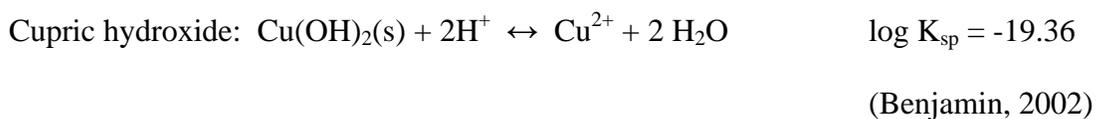
Cupric phosphate: $Cu_3(PO_4)_2 \cdot 2H_2O(s) \leftrightarrow 3Cu^+ + 2PO_4^{3-} + 2H_2O$ $\log K_{sp} = -38.76$

(Schock et al., 1995).

Schock et al. (1995) further propose that the solubility of the $Cu_3(PO_4)_2$ scale, and

therefore, the effectiveness of orthophosphate as an inhibitor, is determined by the

relationship between the system's pH, dissolved inorganic carbon, and orthophosphate

concentration. As a result, the total solubility for copper (II) in that system can be

expressed:

$S_{tot, Cu (II)} = S_{Cu (II), OH} + S_{Cu (II), CO3} + S_{Cu (II), PO4}$

where

$S_{tot, Cu (II)}$ = total soluble copper
$S_{Cu (II), OH}$ = soluble cupric hydroxide
$S_{Cu (II), CO3}$ = soluble cupric carbonate
$S_{Cu (II), PO4}$ = soluble cupric phosphate

While the theory of a $Cu_3(PO_4)_2$ scale reducing copper solubility is generally accepted,

there is little research available that relates scale composition, which may be determined

by analyzing the copper pipe surface, to solubility (Zhe and Pehkonen, 2004).

A series of surveys of U.S. drinking water providers between 1994 and 2001

indicate that between 38 and 72 percent of the utilities surveyed were adding phosphate

to inhibit corrosion, and over 80 percent of those utilities cited lead or copper control as

the reason for the phosphate addition (McNeill and Edwards, 2002). McNeill and

Edwards (2002) interpreted those survey responses to suggest that many of the utilities

are using phosphate doses based on anecdotal recommendations or vendor data, without a

scientific basis, in order to obtain copper and lead concentrations below the action levels

established by the 1991 LCR. In addition to the LCR's guidelines, the USEPA's 2003

Groundwater Rule required many smaller (previously exempt) utilities to begin

chlorination.   Studies have shown that chlorination will increase water's corrosiveness

due to the chlorine's strong oxidation potential, particularly at lower pH levels where

hypochlorous acid is the dominant species (Cantor et al., 2003). When a chlorine

residual is mandated, and the elevated chlorine levels resulted in a soluble copper

increase, Cantor et al. (2003) have demonstrated the effectiveness of orthophosphate to

reduce copper solubility.

Despite the fact that many utilities were basing phosphate-treatment decisions on

anecdotal evidence or trial-and-error dosing approaches, a relationship between actual

phosphate dosage and soluble copper measurements began to emerge. Data from field

measurements and over a decade of empirical research suggest a correlation between

phosphate concentration and reduced copper solubility under certain environmental

conditions. In a highly-controlled laboratory pipe-rig experiment, orthophosphate

reduced copper solubility under all conditions tested, with the exception of pH 7.2 in very

new copper pipes and pH 7.2 in high-alkalinity, old copper pipes (Edwards et al., 2002).

Dartmann et al. (2004) compiled a comprehensive review of earlier lab results dating

back to the 1980s that generally confirm that orthophosphate addition lowers copper

solubility in neutral pH ranges. However, based on pipe-rig experiments conducted by

Dartmann et al. (2004) as part of the same study, it was found that at low pH,

orthophosphate dosage can lead to an increase in copper solubility. On a series of pipe-

rig tests using high-alkalinity Wisconsin groundwater from two similar communities,

orthophosphate appeared to reduce soluble copper levels for one community's water,

while slightly raising the solubility in the second (Cantor et al., 2000). Researchers in this experiment noted that differences in water quality (pH, temperature, bicarbonate levels, dissolved oxygen, chlorine, nitrate, and sulfide) as well as the different ages of the copper pipes may be potential causes for this disparity (Cantor et al., 2000). On a larger scale, a pilot-scale water distribution test conducted on pipe loops at Seymour Lake, Vancouver, yielded similar results: zinc orthophosphate generally lowered soluble copper levels, although the orthophosphate's effectiveness appears to be sensitive to pH (Churchill et al., 2000). Finally, in a nation-wide study, a 1992 American Water Works Association survey of 361 utilities made the following observations about the effect of orthophosphate addition on copper solubility (Dodrill and Edwards, 1995):

- increasing pH reduces solubility whether or not orthophosphate is used;

- the effectiveness of orthophosphate addition is limited in low alkalinity (<30 mg/L as $CaCO_3$), low pH (<7.0) and high alkalinity (>90 mg/L as $CaCO_3$), high pH (>7.8) waters;

- the optimal orthophosphate dosage is highly pH-dependent; low pH (below 7.0) can reduce inhibitor effectiveness, while inhibitor can actually increase copper solubility above pH 7.8, depending on alkalinity characteristics

In summary, use of orthophosphate by U.S. utilities during the past decade appears to have had a beneficial result in terms of copper corrosion control, though further study is needed to define and better understand the precise conditions, mechanisms, and limitations of this control method.

2.5. Orthophosphate-Copper Solubility Models

The tendency of a solid copper compound to dissolve into solution is characterized by that solid's equilibrium *solubility product*, K_{sp}. The following chemical equation is for the dissolution of solid cupric hydroxide:

$$Cu(OH)_2(s) \leftrightarrow Cu^{2+} + 2OH^-$$
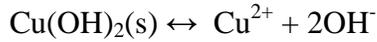
K_{sp} is defined as the product of the activities of the dissolved species on the right-hand side of the equation, divided by the activity of the solid on the left-hand side of the equation (which, by definition, is 1). Thus, $K_{sp} = \{Cu^{2+}\}\{OH^-\}^2$, where $\{x\}$ is the activity of x. Activity of any species in the system can be determined by multiplying that species' concentration by an activity coefficient (which can be calculated based on solution ionic strength) (Benjamin, 2002). Thus, by measuring the concentrations of the dissolved species on the right-hand side of the equation, one can calculate an activity quotient, Q, which equals the product of the activities of the reaction products. A comparison between Q and K_{sp} can then predict whether copper will tend to precipitate (if $Q > K_{sp}$) or dissolve (if $Q < K_{sp}$) in a particular system (Benjamin, 2002). To determine the effect of orthophosphate as a corrosion inhibitor, one must consider the relative K_{sp} of the copper-orthophosphate species formed after orthophosphate addition, to the K_{sp} of the solid species in the system prior to the orthophosphate addition. In other words, for the orthophosphate to effectively lower the level of soluble copper in solution, the following relationship would have to be valid for the system:

K_{sp} (PO_4 scale) $< K_{sp}$ (natural scale), given:

- K_{sp} (PO$_4$ scale) = solubility product of cuprous phosphate, or whichever

phosphate species is found to dominate on the interior pipe surface following

phosphate addition;

- K_{sp} (natural scale) = solubility product of cuprous hydroxide, or whichever solid

copper species dominates the interior pipe surface prior to phosphate addition.

In an effort to explain the observed effects of orthophosphate on copper solubility,

and to make useful recommendations to utilities considering a phosphate regimen, several

copper solubility models have been developed and refined during the past two decades.

The USEPA's cupric hydroxide model is based on the premise that equilibrium between

solid cupric hydroxide ($Cu(OH)_2(s)$) scale and drinking water is the controlling reaction

governing the level of soluble copper (II) in drinking water systems (Schock et al., 1995).

Under this premise, the K_{sp} of the copper-orthophosphate compound formed after

orthophosphate addition would have to be lower than the K_{sp} of cupric hydroxide in order

for the orthophosphate treatment to be an effective option. Schock et al. (1995)

demonstrated that copper solubility is better predicted under this model as a function of

pH and dissolved inorganic carbon (DIC) than under previous models which assumed

malachite ($Cu_2(OH)_2CO_3$ (s)) to be the solid scale that governs dissolved copper

concentrations at equilibrium. Under the cupric hydroxide model, the addition of a 1-5

mg/L dose of orthophosphate may allow effective copper corrosion control at a neutral

pH (7.2 – 8.0) (Schock et al., 1995). Without the inhibitor, a pH adjustment above the

neutral range would be required for similar control.   Schock et al. (1995) acknowledge

that additional experimental confirmation of the orthophosphate solubility constants are

required to refine the model's precision, and point out that the aging process, in which cupric hydroxide is superseded by less soluble solid species, may reduce the orthophosphate's effectiveness.

A 2001 pipe-rig experiment comparing copper solubility at various pH, alkalinity, pipe ages, and orthophosphate levels supported the cupric hydroxide model's predictions (Edwards et al., 2001). Edwards et al. (2001) reported a strong correlation ($R^2 = 0.91$) between the effects of orthophosphate on old pipes and the effects of the same levels of orthophosphate on new pipes. This correlation suggests the tendency of orthophosphate is to reduce corrosion regardless of pipe age, although the model consistently under-predicted measured copper solubility by 60%, leading the researchers to suggest a kinetic limitation, or a solubility product value in the model that differed from the empirical observations. A related experiment comparing predictive model results against observed copper solubility measurements verified that the cupric hydroxide model will accurately predict solubility near pH 7, but under-predict solubility at higher pH levels (Edwards et al., 1996). Edwards et al. (1996) attribute this discrepancy to the fact that the cupric hydroxide model inadequately accounts for effects of high alkalinity at these pH levels.

2.6. Summary

Copper will be used as a drinking water plumbing material for the foreseeable future due to its attractive properties. As with any metal, copper piping will corrode in the presence of oxidizing agents, and over time, through a combination of corrosion and scale formation, will reach an equilibrium condition with the drinking water it contacts, releasing soluble copper into that water. Although not as significant a human health

concern as lead, copper is receiving increased attention by the USEPA, and LCR-mandated action levels have prompted US utilities to focus attention on copper corrosion reduction strategies. One increasingly common strategy is the addition of orthophosphate into the drinking water to serve as a corrosion inhibitor. Although orthophosphate use is on the rise, there is still little definitive scientific research that can predict or prescribe the required dose to treat specific water systems. Recent laboratory and pilot plant observations indicate a correlation between orthophosphate dosage and copper solubility, although the orthophosphate appears to function best within a limited pH and DIC range. The USEPA's cupric hydroxide model appears to be a good predictor of copper solubility based on pH, DIC, and orthophosphate levels; however, limited research has been done relating the chemical equilibrium equations used by the model with the actual solid species determined to be present in the scale. This research is intended to evaluate the cupric hydroxide model's ability to predict the impact of orthophosphate on soluble copper by examining the effect of orthophosphate addition on water chemistry and solid scale in copper pipe, and to evaluate the relationship between orthophosphate concentration and development of solid scale on the pipe surface. The experimental approach to be used to evaluate the model based upon the observed water and solid chemistry is presented in Chapter III.

III. Experimental Materials And Methods

3.1. Introduction

WPAFB draws approximately one billion gallons of drinking water from the Great Miami Buried Valley Aquifer annually, through a network of six well systems. Treatment includes air stripping, CO_2 injection for pH reduction, chlorination, and fluoridation before the water enters the base distribution lines (Shaw, 2005). Based on monthly water quality records from November 2005 through July 2006 (Appendix A), the drinking water on WPAFB, Area B, has the following chemistry: pH range of 7.2-7.5; high alkalinity, ranging from 270-300 mg/L as $CaCO_3$; fluctuating hardness, ranging between 20-250 mg/L as $CaCO_3$; a total phosphorus level ranging between 0.16 and 0.63 mg/L; and a free chlorine residual level ranging between 0.56-0.72 mg/L.

Building 20630, the Wright Care CDC, was constructed in 2000. In June and July 2004, a drinking water survey of the CDC revealed high levels of copper: the average total copper concentration was 1.59 mg/L, as nearly one-third of the 159 taps sampled exceeded the 1.3 mg/L LCR action level (Shaw, 2005). These elevated copper levels drew considerable interest due to health care concerns for the young children who were the primary building occupants. As an interim control measure, the facility managers were instructed to flush every drinking water tap in the building for at least 30 seconds at the start of each business day.

As a long-term solution, WPAFB contracted for the installation of an orthophosphate injection system in the utility room of the CDC. This system was intended to reduce copper concentration throughout the facility's drinking water system

using a demand-driven injection of orthophosphate solution. A photo of the installed

system is provided in Figure 2.

Figure 2. Orthophosphate Injection System, Bldg 20630

Components of the system included a 55-gallon barrel used to mix and store the

orthophosphate solution; a feed pump (LMI Model #AA771-358SI) used to deliver the

orthophosphate solution at a constant, demand-driven flowrate; and an injection port into

a three-inch copper loop, configured as a bypass at the drinking water service entrance to

the facility. The orthophosphate used in the system was a one percent (wt/wt) disodium

phosphate dihydrate solution ($Na_2HPO_4 \cdot 2H_2O$). The flowmeter was initially set to inject

1.5 mg/L. Periodic adjustments were made, increasing the flow to 1.9, then 2.0 mg/L by

July 2006, in order to sustain an orthophosphate concentration of at least 1.0 mg/L in the building's water distribution system.

3.2. Methodology

The methodology followed in this research can be categorized into four processes:

A. Water sample collection and analysis – the process used to obtain water samples and characterize their chemical composition;

B. Jar tests – the process used to develop standardized curves to define the expected relationship between pH, orthophosphate, and copper concentration;

C. Solids sample collection and analysis – the process used to obtain copper pipe samples and characterize their surface solids; and

D. Prediction of orthophosphate effectiveness using equilibrium models and comparison of model predictions with field results.

Details of each of these processes are provided in the following subsections.

3.2.1. Water Sampling & Analyses.

Sampling for water quality is based on a schedule designed to characterize the water both before and after the orthophosphate system installation, from multiple locations inside the CDC. The three variables to be established for this methodology included: 1) sampling frequency; 2) sampling locations; and 3) required analyses. Sampling was conducted at different frequencies, during each of three phases of the investigation. In the first phase, between October and December 2005, prior to the orthophosphate system installation, sampling was conducted on a weekly basis, in order to ensure at least nine data points were available to serve as a water quality baseline

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against which later measurements could be compared. Following the installation of the orthophosphate system, biweekly sampling was conducted for four months, until the system appeared to reach a stable target level for copper concentration. At that point, the third phase commenced, when sampling frequency was reduced to a monthly follow-up, in order to ensure that longer-term copper levels were remaining stable. A key element of the sampling schedule was the flushed and stagnant protocol followed during each of the three phases; regardless of the sampling frequency, all samples involved the collection of a flushed sample taken at 1700 hrs at the end of each business day, coupled with a stagnant sample collected prior to the start of business the following morning (0600 hrs), ensuring a twelve-hour stagnation time. Sampling locations were selected in order to best characterize the water throughout the building. A central location was selected to measure water quality in the building distribution system shortly after the water entered the facility. In addition, locations were selected at the far end of the distribution system in each of the two building wings, on both the north and south side of the facility. The goal of this sampling location plan was to compare copper levels of water shortly after entry into the facility against the copper levels of water that has traveled to the terminal ends of the drinking water distribution systems. The five locations that were sampled during weekly baseline sampling are identified in Figure 3.
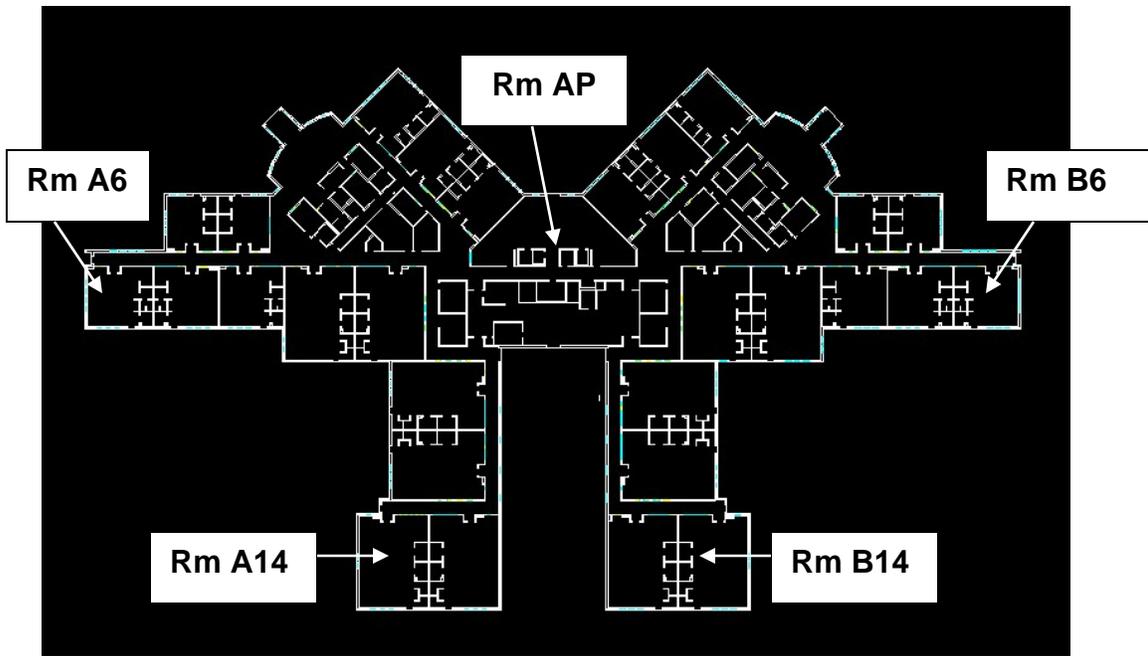
Figure 3. Initial Weekly Water Collection Locations, WPAFB CDC

During subsequent phases, the three locations shown in Figure 4 were used for sampling:
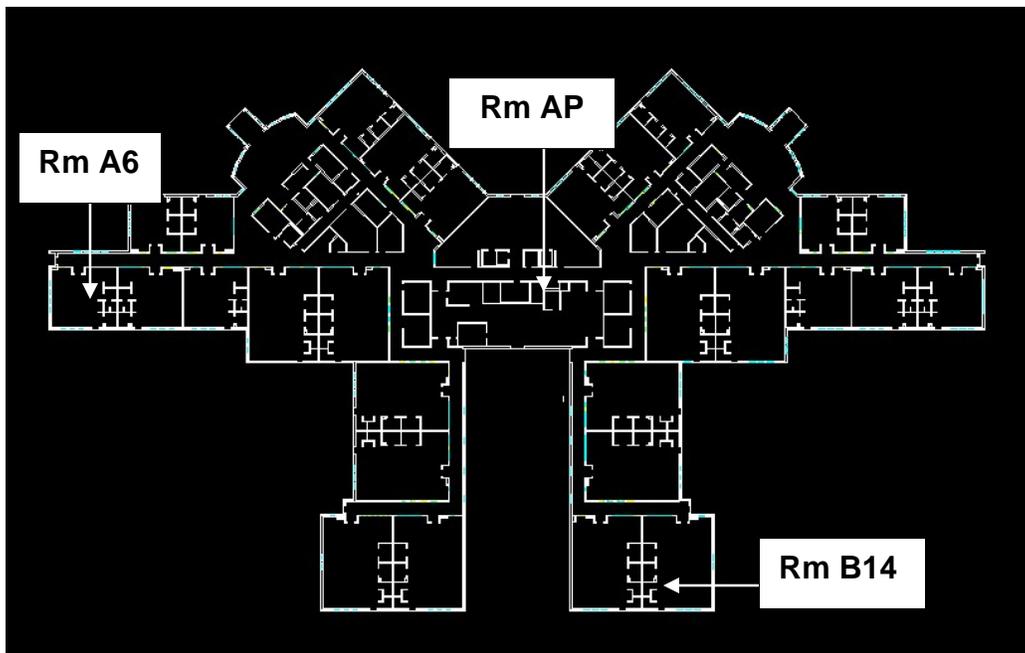
Figure 4. Follow-on Water Collection Locations, WPAFB CDC

The reduction from five to three sampling locations was based on the observation that very similar results were obtained from sampling points B6 and B14 and from sampling points A6 and A14.

The analyses conducted for this experiment were selected in order to provide relevant information to determine the effect and characterization of orthophosphate-copper reactions. Wet chemistry analyses, performed within 24 hours at an off-site laboratory, included copper concentration, orthophosphate concentration, total phosphate concentration, and total alkalinity. Field measurements, performed within 30 minutes of sample collection at the Air Force Institute of Technology laboratory, include temperature, pH, dissolved oxygen, total chlorine, and free chlorine. These nine measurements provided the data necessary to determine the effectiveness of the orthophosphate's control of copper concentration, as well as the ability to characterize the relevant reactions. The data also provided input parameters for later use in equilibrium solubility models.

Laboratory wet chemistry analysis was performed according to USEPA-approved methods. Copper analysis was conducted using an inductively coupled plasma mass spectrometer (ICP-MS) procedure IAW EPA method 200.8. Total phosphorus and orthophosphate analyses were performed using colorimetric spectroscopy IAW EPA method 365.4. Total alkalinity analysis was performed using a titration procedure IAW EPA method 310.1 and standard method 2320B.

In order to analyze the effect of stagnation time on copper corrosion, a series of samples were collected from a single tap (Rm AP) in the CDC over a three-day period in September 06, after the orthophosphate system had been operating for seven months. A

baseline sample was collected after the tap was thoroughly flushed for 3 minutes. A first-draw (250 mL) and second-draw (250 mL) sample was collected and prepared for storage. The faucet was covered and taken out of service for the next three days. Follow-on first-draw and second-draw samples were taken after a stagnation time of five hours, ten hours, twenty-four hours, and seventy-two hours.

3.2.2. Jar Tests.

A series of jar tests was performed in order to establish the relationship between pH and copper solubility, along with the dose-response relationship between orthophosphate and dissolved copper. Four liters of water were collected from the building adjacent to the WPAFB CDC; this water was selected as a representative sample of WPAFB drinking water prior to addition of orthophosphate. To develop a pH-response curve, one liter of the sample water was spiked with a 15 mg/L copper stock solution and titrated with 0.1M HCl through a range of pH 6.5 through pH 8.9. To develop an orthophosphate dose-response curve, one liter of the sample water was spiked with a 6.0 mg/L copper stock solution, then sodium phosphate solution was added incrementally. The water was maintained at pH 7.50 (+/- 0.1) by acid/base titration throughout the orthophosphate addition. The orthophosphate was added in increments ranging from 0 to 4.2 mg/L in a series of five experiments. Copper and orthophosphate concentrations were measured using methods 135 and 490, respectively, on a Hach 2000 DR colorimeter. The results of the two jar test curves are provided in Chapter 4. These standardized curves are required to analyze the effect of the orthophosphate corrosion inhibitor used in the CDC.

3.2.3. Solids Sampling & Analysis.

To analyze the surface characteristics of the copper pipe in the WPAFB CDC, samples of the pipe were removed from the facility for X-ray diffraction (XRD) spectroscopy and stereo-microscopic inspection. Six-inch segments of copper pipe were removed from horizontal runs in the distribution system immediately adjacent to sampling locations A6 and B14. Small chips were then cut from the bottom and top of these samples in preparation for XRD and stereomicroscopic analysis. These samples were collected twice: first, in December, 2005, prior to the orthophosphate treatment, and again in October, 2006, after the orthophosphate system had been operating for approximately eight months. Analysis was performed in the USEPA water research laboratories, Cincinnati.

3.2.4. Copper Solubility Model Application.

3.2.4.1. USEPA Cupric Hydroxide Model.

The cupric hydroxide model developed by the USEPA (see Section 2.5) allows the user to specify precipitation reactions in order to predict equilibrium concentrations of individual species within a system. To determine the effects of increasing orthophosphate on copper concentration, the model was constructed with the following thermodynamic constants:

Table 1. Thermodynamic Constants in Cupric Hydroxide Model

Species	Log K or Log β value
$CuOH^+$	-7.96
$Cu(OH)_2$	-14.1
$Cu(OH)_3^-$	-26.9
$Cu_2(OH)_4^{2-}$	-39.56
$Cu_2(OH)_2^{2+}$_	-10.58

$Cu_3(OH)_4^{2+}$	-20.76
$CuCO_3$	6.73
$Cu(CO_3)_2^{2-}$	10.6
$CuHCO_3^+$	12.13
$Cu(OH)CO_3^-$	-4.25
$Cu(OH)_2CO_3^{2-}$	-13.14
$CuH_2PO_4^+$	15
$CuHPO_4^0$	16.35
$Cu(OH)_2$ (s)	8.89
$Cu_3(PO_4)_2$ (s)	-38.76

(Schock et al., 1995 (Table 3))

In addition, the dissolved inorganic carbon (DIC) concentration was specified as 73 mg

C/L, based on the typical alkalinity of 280 mg/L as $CaCO_3$ and pH of 7.5 observed in the

WPAFB CDC. pH for each of the simulations was specified over the range pH 6.0 – pH

10.0, with calculations reiterated in 0.1 pH increments. The model simulation results

pictured in Figure 5 required seven simulations: the solid species and orthophosphate

parameters for each of the seven simulations are identified below:

Table 2. Parameters Used During Cupric Hydroxide Model Simulations

Simulation	Possible Solids	$[PO_4^{3-}]$ (mg/L)
1	$Cu(OH)_2$	0.0
2	$Cu(OH)_2$, $Cu_3(PO_4)_2$	0.5
3	$Cu(OH)_2$, $Cu_3(PO_4)_2$	1.0
4	$Cu(OH)_2$, $Cu_3(PO_4)_2$	2.0
5	$Cu(OH)_2$, $Cu_3(PO_4)_2$	3.0
6	$Cu(OH)_2$, $Cu_3(PO_4)_2$	4.0
7	$Cu(OH)_2$, $Cu_3(PO_4)_2$	5.0

When no orthophosphate is present, the only solid specified is $Cu(OH)_2$(s). As

orthophosphate concentration is increased, $Cu_3(PO4)_2$(s) is introduced as an additional

species. The results of these simulations are pictured below in Figure 5, with each curve

representing theoretical dissolved copper concentration vs pH for seven specific

orthophosphate concentration levels:
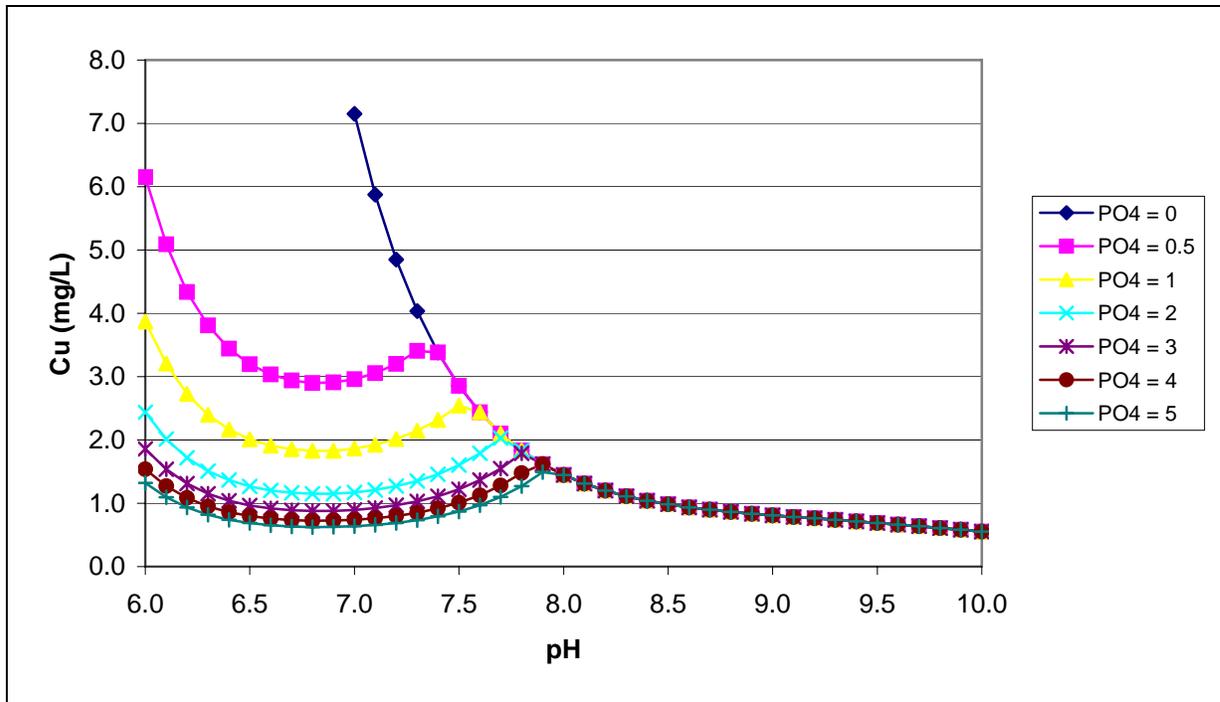
Figure 5. Cupric Hydroxide Model Results: Cu (mg/L) vs pH

To focus on the specific pH level typically observed at the WPAFB CDC (pH = 7.5), the

copper concentration from Figure 6 was plotted against each orthophosphate

concentration at pH 7.5, yielding the following curve:
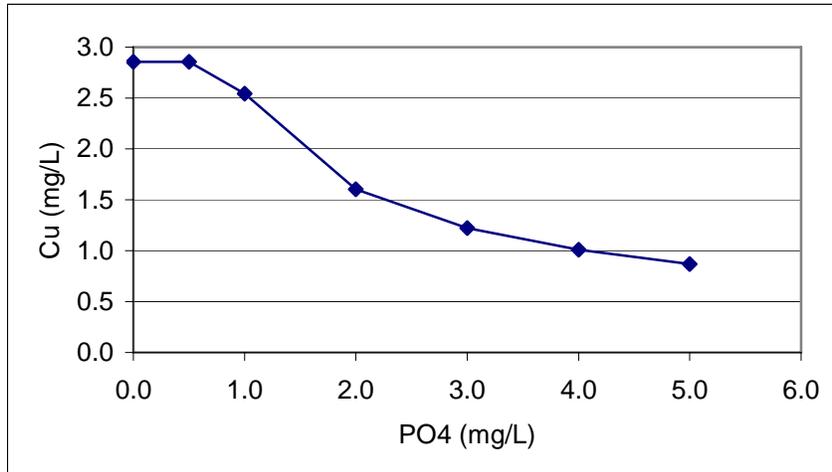
Figure 6. Cupric Hydroxide Model Results: Cu vs PO4 (mg/L)

A comparison of the cupric hydroxide model's outputs to field measurements from the WPAFB CDC is included in Chapter IV.

3.2.4.2. VMINTEQ Model

Visual MINTEQ, version 2.40, (VMINTEQ) provides another model against which the field measurements for this research could be compared. VMINTEQ is a chemical equilibrium program designed to access a large thermodynamic database. It was initially developed by the USEPA in 1997, and it has been continually updated by the Swedish Research Council and Foundation for Strategic Environmental Research (Gustafsson, 2004) during the past decade. Gustafsson reports that while the program is commonly used to model the speciation of dissolved ions in water, it can also be used to model precipitation/dissolution reactions and titrations. The VMINTEQ model can be used to simulate the reactions for multiple species under a wide variety of water quality conditions, allowing predictions for complex systems.

For this research, two models were developed: one model to replicate the conditions present during the standardization jar tests, as described in section 3.2.2; a second model to simulate conditions encountered in the field system measured in the WPAFB CDC.

Jar Test Simulation Model

For the first VMINTEQ model, the goal was to predict dissolved copper concentrations observed in the laboratory jar tests as a result of orthophosphate addition. Therefore, the following water quality assumptions were used to develop the model:

- Chlorine: set to 0.000002M (typical CDC free chlorine residual = 0.07mg/L)

- Na^+: set to 0.0065M (typical Area B water quality levels = 150 mg/L)

- Alkalinity: set to 0.0057M as HCO_3^- (Area B alkalinity = 280 mg/L as $CaCO_3$)

- pH: the model was run at three pH levels, bracketing the typical observed

values at the CDC: pH 6, pH 7, pH 7.5

During the jar test, the sample water was not exposed to the solid scale that would be encountered in a copper pipe system as it was tested in a glass cell. However, VMINTEQ allows the user to identify possible solid species, and therefore, both $Cu(OH)_2(s)$ and $Cu_3(PO_4)_2(s)$ were specified as possible species in the model. In order to provide dissolved copper for the test, the sample water was spiked with a cupric perchlorate solution. Therefore, in the VMINTEQ model, the following component concentrations were used, based on the jar test concentration of the copper perchlorate:

- Cu^{2+}: set to 0.000118M (based on 7.7 mg/L $Cu(ClO_4)_2$ in jar test)

- $(ClO_4)_2$: set to 0.000236M (based on 7.7 mg/L $Cu(ClO_4)_2$ in jar test)

The VMINTEQ model was used to evaluate the effect of various levels of orthophosphate on the dissolved copper. Therefore, during the model simulations, PO_4^{3-}

was added incrementally, in 100 steps of increasing concentration, from 10^{-6} M to 10^{-4} M.

The PO_4^{3-} was added in the form of sodium phosphate $(Na_3(PO_4) \cdot 12H_2O)$. As the

background concentration of Na^+ ions in the model had been defined as 0.0065M, the

additional 3×10^{-4} M Na^+ added at the highest orthophosphate increment $(10^{-4}$ M) was

assumed insignificant (<5% of Na^+ in solution), so increments of Na+ were not simulated

in the model. Results of this model are shown in Figure 7 for three different pH levels.
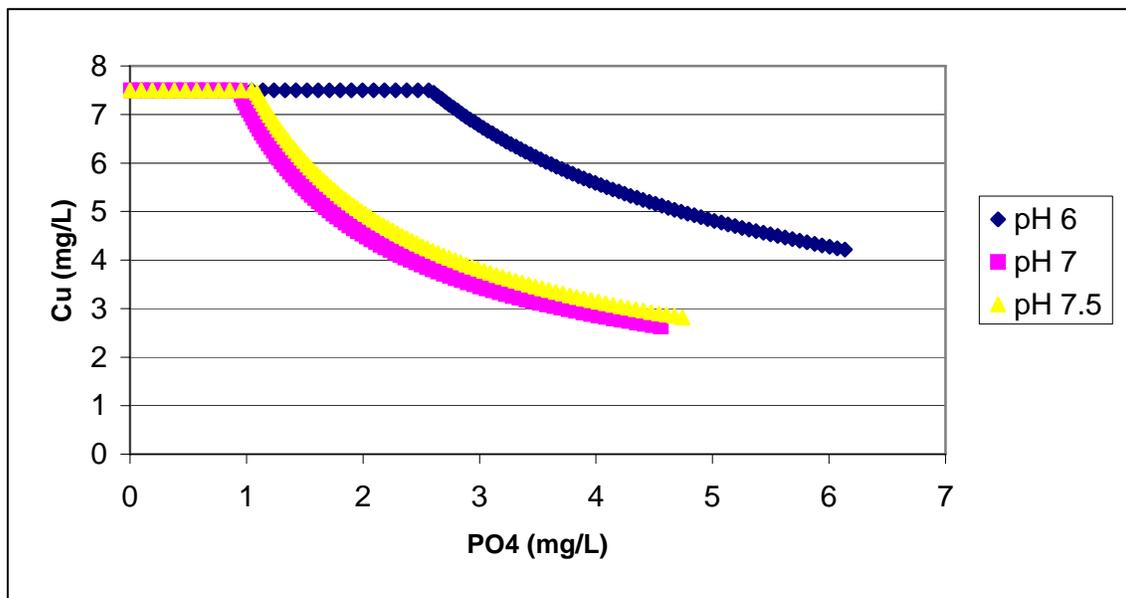
Figure 7. VMINTEQ Model Results: Jar Test Simulation

Note the horizontal lines in Figure 7 at the lower end of the phosphate range, for each of

the modeled pH values. These lines indicate that below a certain pH-dependent

phosphate concentration, addition of small quantities of phosphate have no effect on the

dissolved copper concentration. The phosphate concentration at which the added PO_4 is

sufficient to cause copper precipitation, resulting in reduced copper concentration, is

indicated by the point at which the curves depart from the horizontal.

The effect of alkalinity on copper concentration may be isolated within the VMINTEQ simulation to expose a relevant phenomenon. When the simulation was run based on the typical high-alkalinity (280 mg/L as $CaCO_3$) conditions observed at WPAFB, as in Figure 7, the predicted equilibrium concentration of copper prior to the addition of orthophosphate was a high 7.5 mg/L. When the model was run using a lower range of alkalinity values, the results appeared as shown in Figure 8.
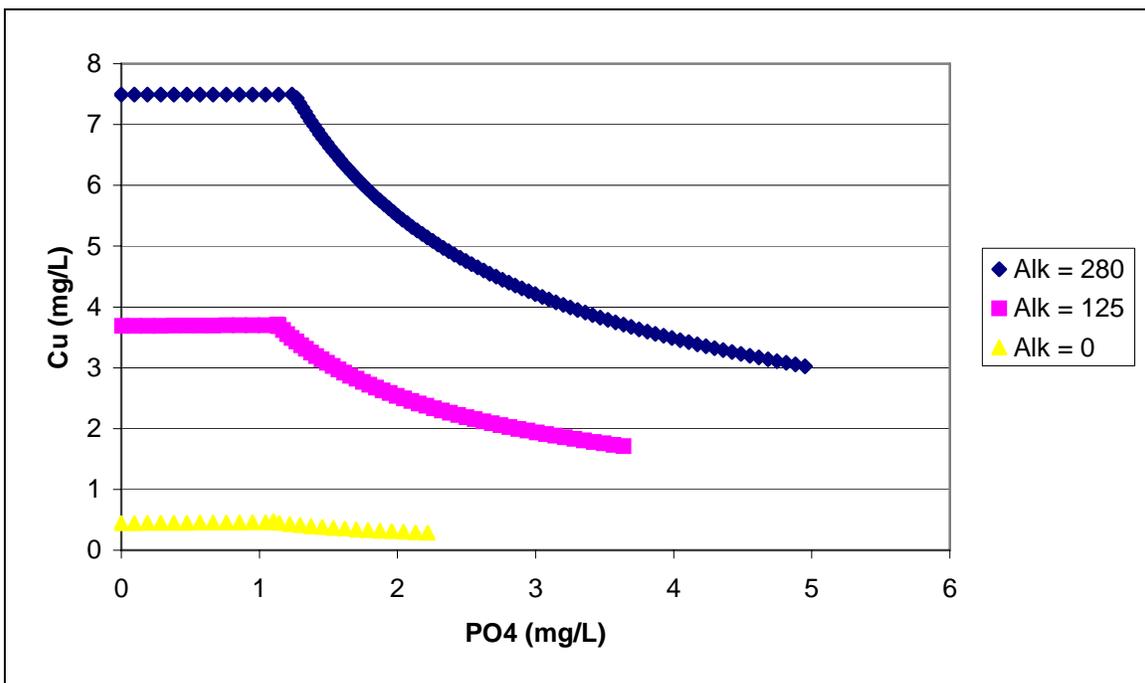
Figure 8. VMINTEQ Results, Effect of Alkalinity (mg/L as Ca CO$_3$)

The impact of increasing alkalinity is clearly illustrated in Figure 8: the high alkalinity levels typical at WPAFB result in an order of magnitude increase in copper concentration at equilibrium in a cupric hydroxide system.

Equilibrium concentration for Cu^{2+} in the absence of orthophosphate can be calculated (see Appendix B). These calculations can be used to help evaluate how the

VMINTEQ code is working, and what thermodynamic parameters are being used. In the simplified calculations, equilibrium with copper hydroxide solid in distilled water at pH 7.5 was assumed, and a solubility product (K_{s0}) of $10^{-19.11}$ was used for the copper hydroxide solid (Schock et al., 1995). We see from Appendix B that the value for the equilibrium copper concentration calculated under these simplifying assumptions is approximately 1 mg/L, while the value predicted by the VMINTEQ model is approximately 7 mg/L (see Figure 7) at PO_4 concentration = 0 mg/L. However, as seen in Table 3, the VMINTEQ model closely approximates the simplified calculations if alkalinity in the model is reduced to the alkalinity (0 mg/L) used in those calculations.

Table 3. Model Predictions Compared to Simple Calculations

Alkalinity	VMINTEQ Prediction	Simplified Calculations
280	7.4 mg/L	-
125	3.8 mg/L	-
0	0.4 mg/L	1.0 mg/L

This correlation suggests that the VMINTEQ output at higher alkalinity levels would also be an accurate prediction of expected copper concentration.

Field System Simulation Model

For the second VMINTEQ model, the goal was to predict the effect of adding orthophosphate on dissolved copper concentrations measured in the field. The following water quality assumptions were used to develop the model:

- Chlorine: set to 0.000002M (typical CDC free chlorine residual $\approx$ 0.07mg/L)

- Na^+: set to 0.0065M (typical Area B water quality levels $\approx$ 150 mg/L)

- Alkalinity: set to 0.0057M as HCO3- (Area B alkalinity ≈ 280 mg/L as $CaCO_3$)

- pH: the model was run at three pH levels, bracketing the typical observed

values at the CDC: pH 6, pH 7, pH 8

This second model does not specify initial copper levels (there is no spiking of cupric

perchlorate in the field measurements), but it assumes the presence of a solid cupric

phosphate scale on the interior of the copper pipe, with cupric hydroxide specified as a

possible solid. Again, PO_4^{3-} is added to the model system in a 100-step incremental

dosage, from 10^{-6} M to 10^{-4} M (as above, the associated increments of Na^+ are

disregarded). The result of this second model for each of three pH levels is shown below

in Figure 9.
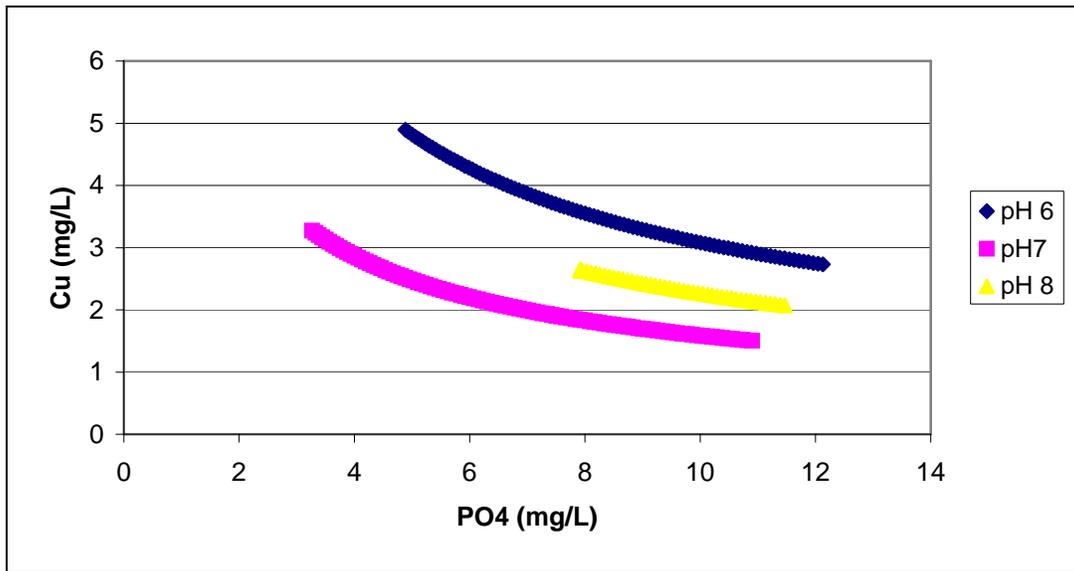
Figure 9. VMINTEQ Model Results: Field Simulation

A comparison of the models' predicted values and actual laboratory/field measurements

is discussed in Chapter IV.

3.3. Sample Collection Protocol

3.3.1. Chemicals and Equipment.

The following chemicals and equipment were used in the collection and analysis of field data described in Sections 3.3.2 through 3.3.4:

- Nitric acid for rinsing and metals sample preservation: *Fisher Scientific nitric acid (OPTIMA grade)*

- Deionized water source: *Millipore Progard II.*

- Orthophosphate for jar tests: Sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) diluted to stock solution, 1 mL/L = 1.38 mg/L

- Copper for jar tests: Cupric perchlorate ($Cu(ClO_4) \cdot 6H_2O$) diluted to stock solution, 1 mL/L = 1.34 mg/L

- Orthophosphate used in bldg 630 corrosion control system:1% disodium phosphate dihydrate solution ($Na_2HPO_4 \cdot 2H_2O$)

- Low-density polyethylene (LDPE) bottles for water sample collection: *Cole Parmer Nalgene LDPE plastic bottles.* Cat no. C-06033-50 (250 mL) and C-06033-20 (125 mL).

- Glass bottles for water sample measurement: *Pyrex*, 250 mL, lot 1395

- Chlorine test kit used in AFIT laboratory: *Hach Pocket Colorimeter II*. Catalog no. 58700-00, lot L4301.

- Dissolved oxygen meter (AFIT lab): *YSI 85 Oxygen, Conductivity, Salinity & Temperature Meter*, model 85/25 FT.

- Direct read meter (USEPA lab): *Hach DR2000 Direct Reading Spectrophotometer.*

- X-ray Diffraction Scope: Scintag (Scintag, Inc., Santa Clara, CA) XDS-2000 theta-theta diffractometer with a copper X-ray tube was used to acquire X-ray patterns.

3.3.2. Water Sampling Collection Protocols.

At each of the water sampling locations identified in Figure 3, the following protocol was observed:

A. For each round of sampling, a primary sampling date (D) was established, and the prior date was identified as day (D-1).

B. Prior to sample collection, field sampling instruments were calibrated in the laboratory. The pH meter was calibrated with 7.0 buffer solution. The YSI dissolved oxygen meter was calibrated according to manufacturer's instructions, using a fifteen minute calibration period and setting the elevation to 700 ft. All LDPE sample collection bottles were flushed with deionized water, then rinsed with a 1+1 nitric acid solution.

C. At 1700 on each day (D-1), the cold-water sample faucet was turned on for one minute. The faucet was turned off, then dried with a paper towel.

D. The LDPE sample collection bottles were filled in the following sequence, as required: 250 mL sample (for copper analysis); a second 250 mL sample (when required for comparative copper analysis); 125 mL sample (for orthophosphate and total alkalinity analysis); 125 mL sample (for total phosphorous analysis). All bottles were capped immediately for transportation to laboratory for additional preparation.

E. 250 mL Pyrex bottle was filled for field analysis of pH, temperature, dissolved oxygen, and chlorine concentration. pH probe was used for direct reading of pH from Pyrex bottle using a one-minute pH measurement. Temperature and dissolved oxygen were measured using YSI dissolved oxygen probe; measurements were based on stabilized readings obtained during one-minute test periods, in which the probe was agitated gently to prevent oxygen depletion at the probe tip. Chlorine residual

concentrations were measured using the Hach Pocket Colorimeter. Two 10-mL glass vials were filled from the Pyrex bottle. The first 10-mL sample is analyzed for free chlorine (free available residual chlorine which has not reacted with anything) following a one-minute reaction time and a DPD Free Chlorine Reagent packet. The second 10-mL sample was then analyzed for total chlorine (total concentration of chlorine in the water, including combined chloroorganics and chloramines, as well as free available chlorine) following a three-minute reaction time and a DPD Total Chlorine Reagent packet. All field measurements were recorded in an experimental notebook.

F. Upon completion of the samples on day (D-1), the faucet was marked with a placard labeled "Do not disturb, sampling in progress," and covered with a clear plastic bag.

G. Steps C through F were repeated for every additional sample faucet location required.

H. At 0600 on each day (D), after twelve hours of stagnation, follow-on samples were collected from every required faucet prior to any flushing of the tap water.

I. After removing the plastic bag and placard, LDPE sample bottles were collected in the following sequence: first-draw 250 mL sample (for copper analysis); second-draw 250 mL sample (when required for comparative copper analysis); 125 mL sample (for orthophosphate and total alkalinity analysis); 125 mL sample (for total phosphorus analysis). All bottles were capped immediately for transportation to laboratory for additional preparation.

J. 250 mL Pyrex bottle was filled for field analysis of pH, temperature, dissolved oxygen, and chlorine concentration; measurements were obtained as per step E above.

K. Steps I through J were repeated for every additional sample faucet location required.

L. Upon return to the laboratory, samples were preserved for further analysis. All copper

samples were acidified with 0.15 percent nitric acid to a pH less than 2.0 IAW EPA

200.7. All total phosphorus samples were acidified with sulfuric acid to pH less than 2.0,

IAW EPA method 365.4. All samples were refrigerated to maintain temperature of 4°C.

3.3.3. Solids Sampling Collection Protocols.

At each of the solid sampling locations identified in Figure 4, the following

protocol was observed:

A. The ceiling panels above each water sampling tap were removed to reveal the

incoming ¾ inch cold water supply line.

B. A six-inch segment was marked on a horizontal pipe section close to the sampling tap.

C. The segment of pipe was removed, placed in a Zip-loc bag and sealed.

D. Steps A through C were repeated for the second sampling location.

E. The pipe segment was cut longitudinally to produce a top and bottom half.

F. Two ¼ inch square chips were cut from the end of each half for XPS analysis.

G. The halves were marked with a designator ("top" or "bottom"), then replaced in the

sealed bags along with their associated chips.

3.3.4. Solids Sample Analysis.

For X-ray Diffraction Spectroscopy (XRD), the following settings were observed:

A. Tube was operated at 30 kV and 40 mA;

B. Scans were typically over the range of 5 to 60 degrees 2 theta, with 0.03 degree step

sizes that were held for 3 seconds each;

C. Pattern analysis was performed using computer software provided by manufacturer,

generally following American Society for Testing and Materials Standards procedures.

IV. Results And Discussion

4.1. Results

4.1.1. Jar Test Relationships: Copper Concentration, pH, and PO₄ Concentration.

The series of jar test standardization experiments indicated that copper solubility

and pH are inversely related (Figure 10).
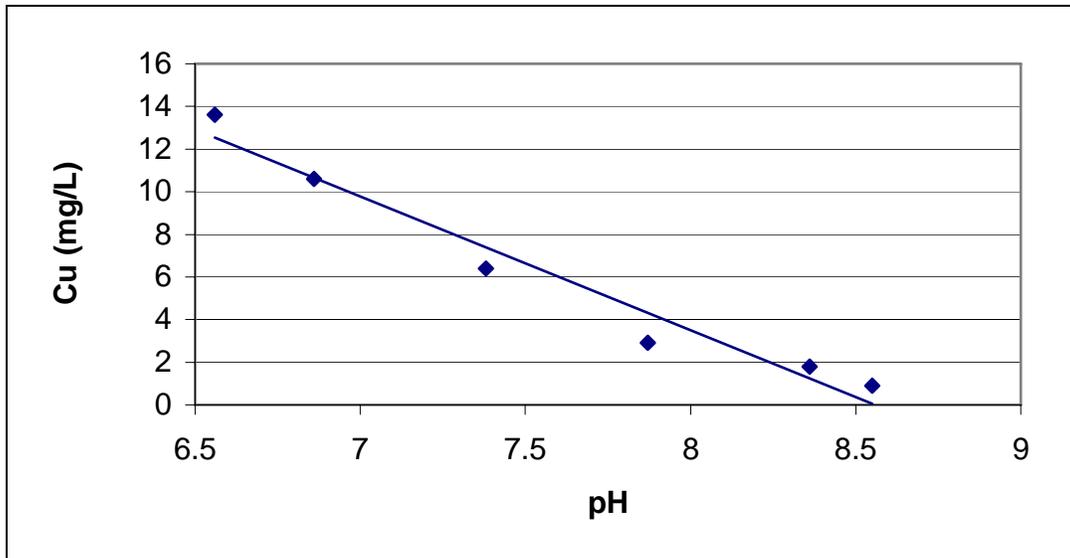
Figure 10. Soluble Copper (0.2 µm filter) vs pH

Linear regression of these data in the mid-pH range suggests a strong inverse relationship

($R^2 = 0.961$), in which a pH increase of 1 results in a 6.3 mg/L decrease in copper

solubility (raw data and regression equations in Appendix C). The jar test results indicate

that a pH of 8.35 would be required to meet the 1.3 mg/L action level maximum for

copper. The relationship between orthophosphate and copper concentration is presented

in Figure 11.
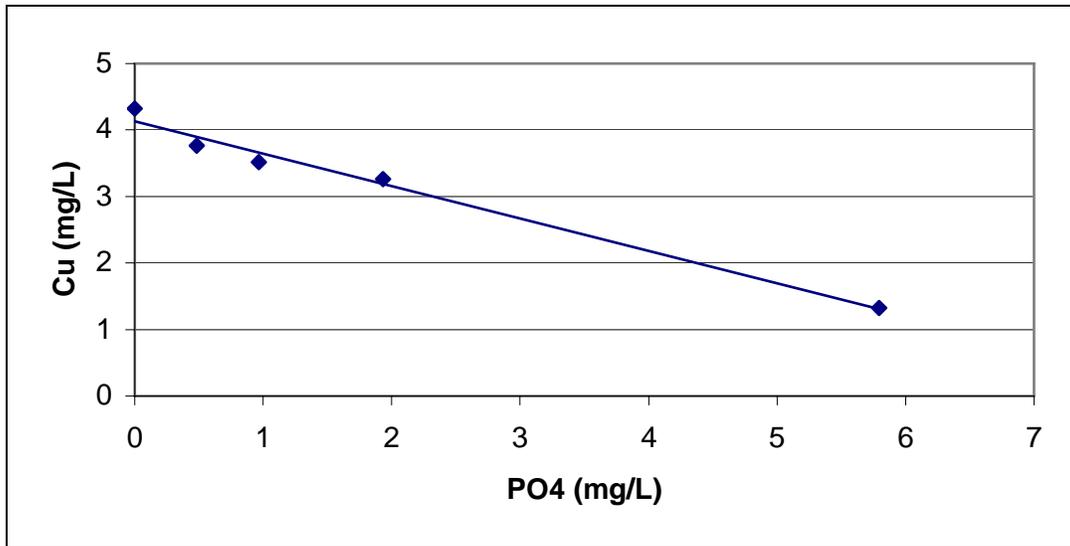
Figure 11. Soluble Copper vs Orthophosphate, pH 7.5

Linear regression of this relationship suggests a strong inverse relationship ($R^2 = 0.985$), where an increase in orthophosphate will result in a decrease of soluble copper concentrations in approximately a 2:1 ratio (1 mg/L PO_4 reduces Cu^{2+} by 0.49 mg/L) (raw data in Appendix D).   The results indicate that an orthophosphate concentration of 5.8 mg/L would be required to meet the 1.3 mg/L action level maximum for copper concentration at pH 7.5.

4.1.2. Field Results: Orthophosphate, Chlorine, and Copper Relationship.

Figures 12 through 17 show the relationship between total copper concentration and orthophosphate concentration in three sampling locations in building 20630. Figures 12, 14, and 16. show the copper concentration after flushing while Figures 13, 15, and 17 show the copper concentration measured after the water remained stagnant for twelve hours. As would be anticipated, copper concentrations after the water was held stagnant were generally higher than the concentrations in the flushed water.
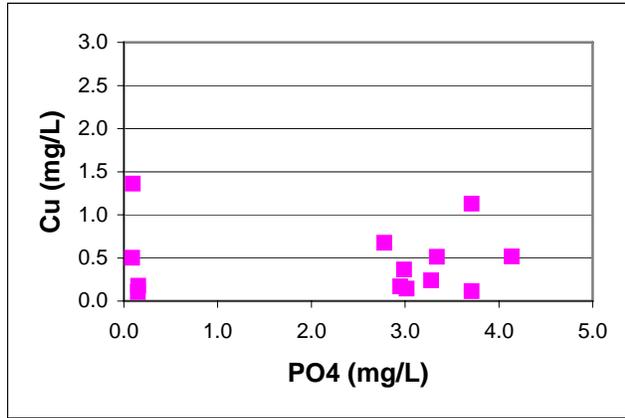
Figure 12. Cu vs PO_4, Stagnant (Rm AP)
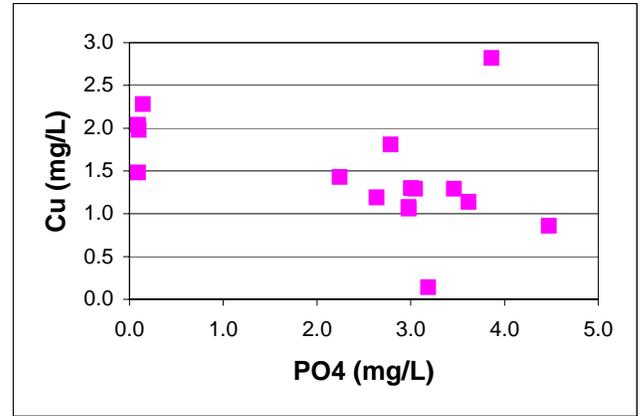
Figure 13. Cu vs PO_4, Flushed (Rm AP)
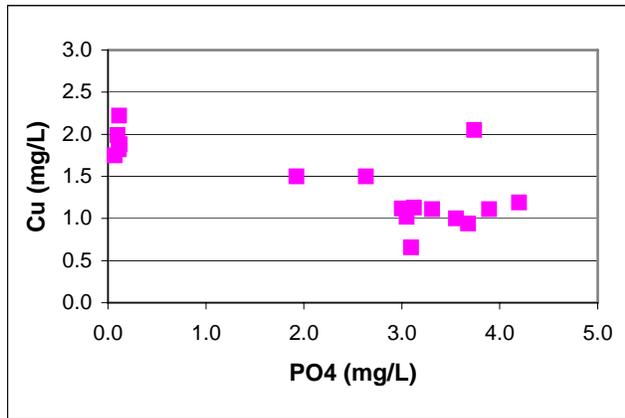
Figure 14. Cu vs PO_4, Stagnant (Rm A6)
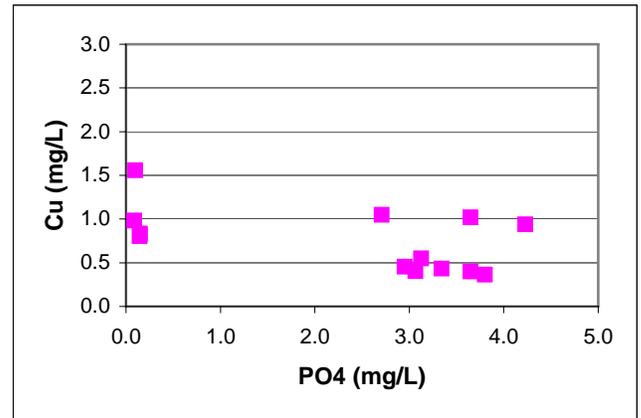
Figure 15. Cu vs PO_4, Flushed (Rm A6)
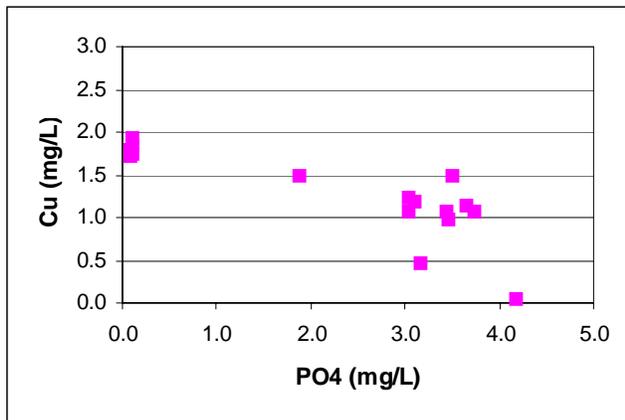
Figure 16. Cu vs PO_4, Stagnant (Rm B14)
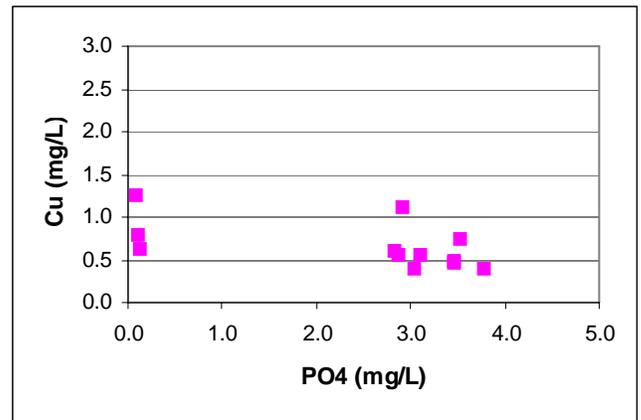
Figure 17. Cu vs PO_4, Flushed (Rm B14)

4.1.3. Field Results: Stagnation Time Relationships.

Figures 18 and 19 show the relationship between chlorine demand, copper concentration, and orthophosphate concentration. The figures present the level of total copper (mg/L), orthophosphate (mg/L as PO_4), chlorine residual following a 12-hr stagnation period (mg/L), and chlorine demand (mg/L). Chlorine demand, shown in the following figures as "Delta Cl", is defined as the difference between the chlorine concentration at 1700 hrs one day and at 0600 hrs the next morning, following a 12-hour stagnation period. Therefore, a negative "Delta Cl" value indicates a decline in chlorine concentration during the stagnation period.   Figure 18 shows free chlorine concentrations; Figure 19, total chlorine concentrations (free and total chlorine concentrations measured as described in Section 3.3.2.)
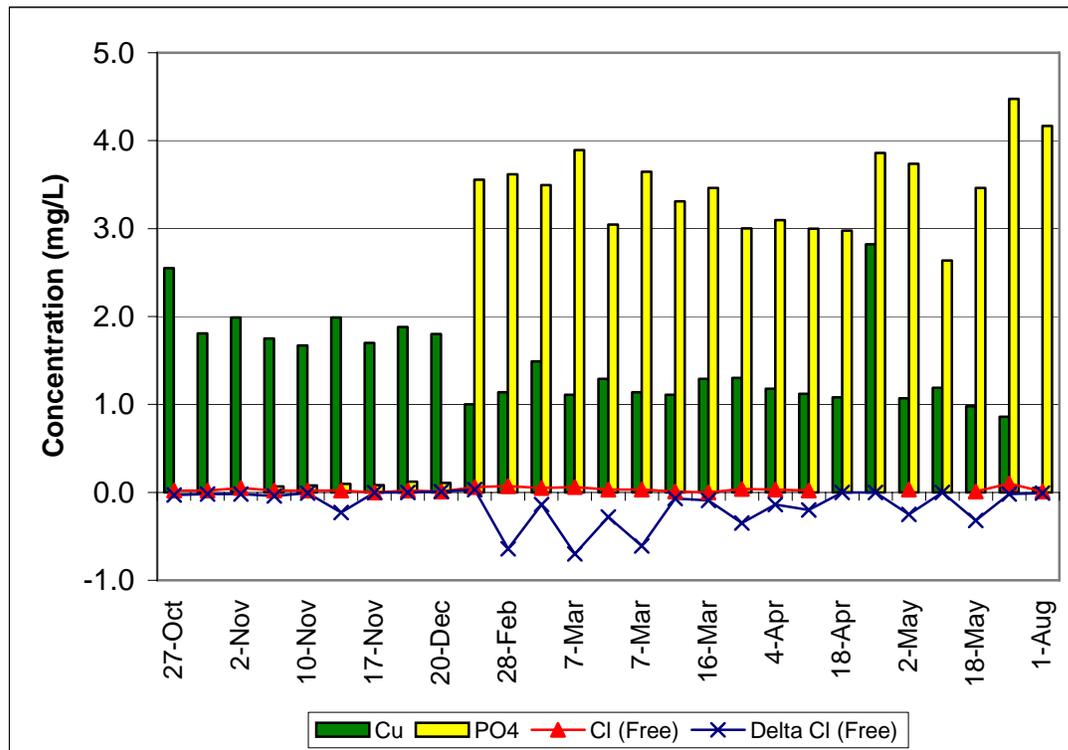
Figure 18. Copper, Orthophosphate and Free Chlorine
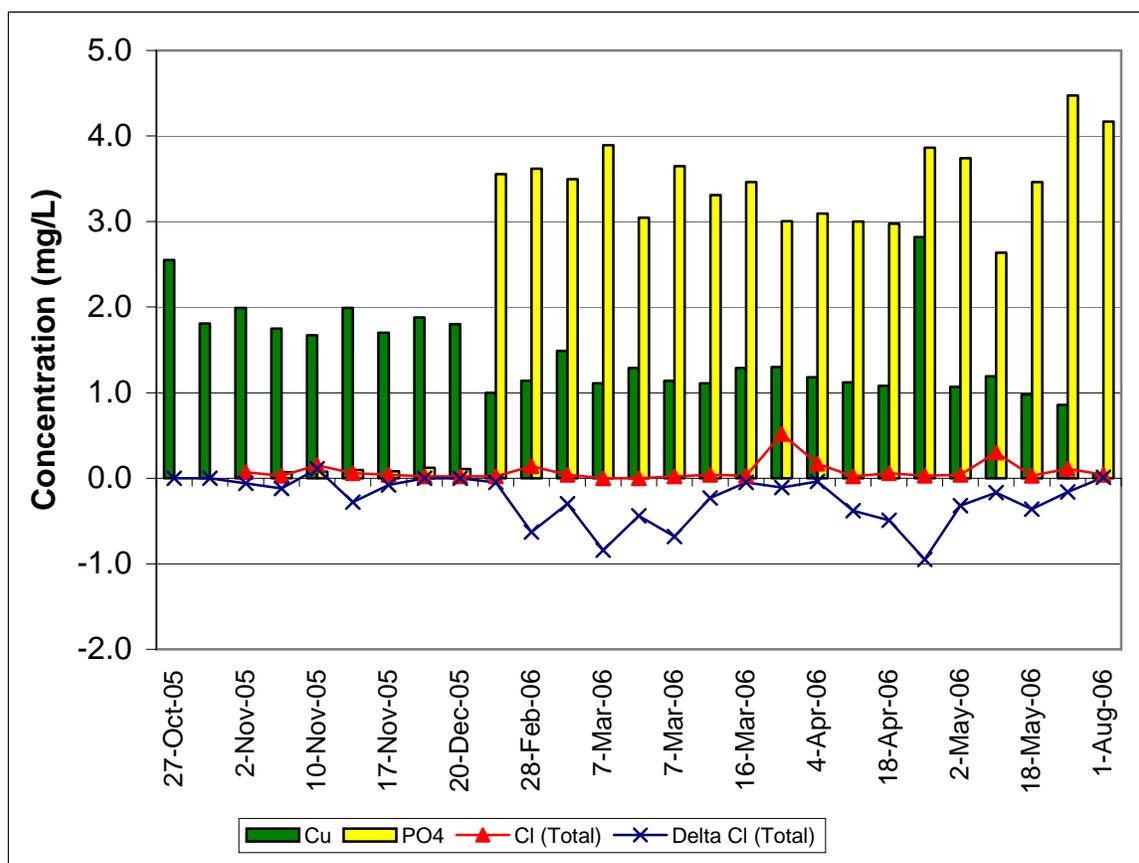
Figure 19. Copper, Orthophosphate, and Total Chlorine

Both free and total chlorine residual data show similar trends. Prior to the

orthophosphate treatment in Feb 06, there were low chlorine residuals and demand: the

chlorine residuals at 1700 hrs each day were already so low that an additional 12 hours of

stagnation did not appear to substantially lower the chlorine levels the next morning.

Immediately after the introduction of orthophosphate, the copper levels declined. It

should also be noted that chlorine demand appears to rise after the introduction of

orthophosphate. In fact, this is the result of a significant increase in residual chlorine

measured in the afternoon flushed water samples (see Figure 20 below), while the 12-

hour stagnant chlorine residual levels remained constant. This suggests that one effect of orthophosphate is a delay in chlorine demand: after orthophosphate treatment, the chlorine residual remained higher in the pipe, as measured during the afternoon sampling. Over the next 12 hours, chlorine concentrations decreased to low levels, which were similar to the levels when no orthophosphate was added.
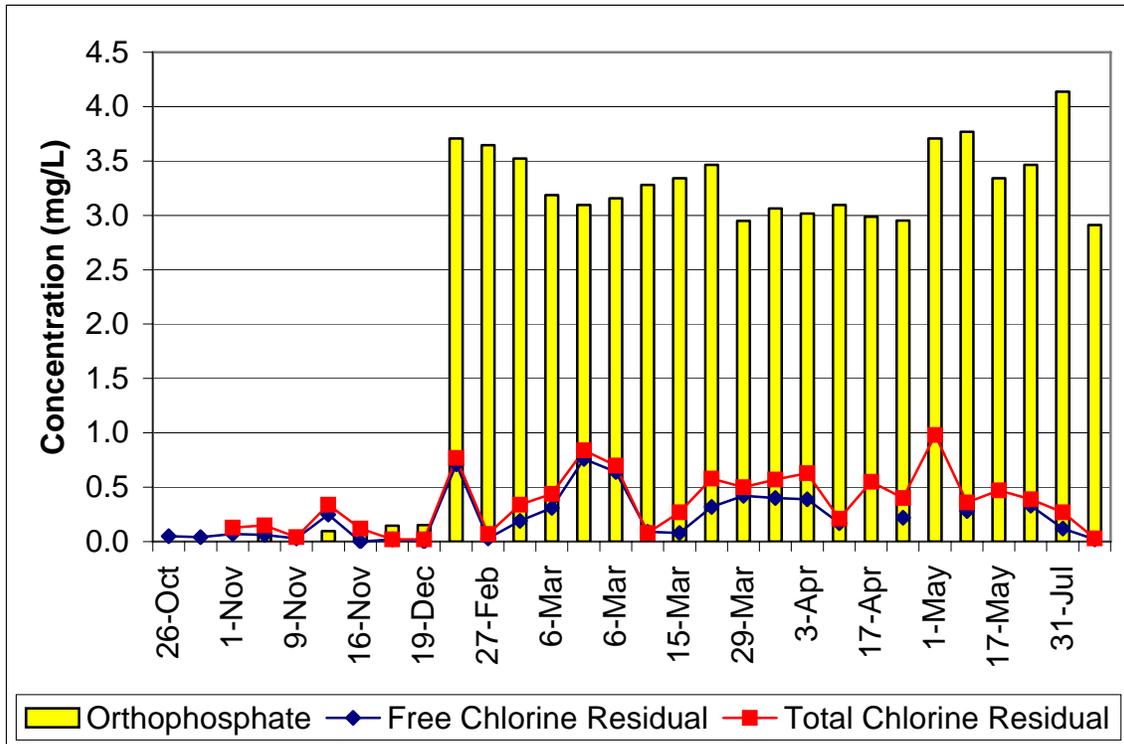
Figure 20. Orthophosphate and Chlorine Residual, Flushed Measurements

The effects of stagnation time on copper and chlorine concentration are shown in Figures 21 and 22, respectively, based on measurements obtained following the standardization experiment procedures described in Section 3.2.1., Figure 21 indicates an increase in copper concentration as stagnation time increases, with the sharpest rise occurring during the first eight hours. The disparity between first and second draw

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samples at four- and eight-hour stagnation times may be due to the fact that while the sample faucet was taken out of service during the sampling period, adjacent water fixtures were in operation. Therefore, the first-draw samples represent true "stagnant" samples, while the second draw may be mixed with some moving water which flowed through adjacent fixtures. After 24 hours, when all facility fixtures had been taken out of operation, copper concentration measures in the first and second draw samples are similar. Figure 22 indicates that chlorine residual levels decrease with stagnation time, with over 90 percent of the residual consumed in the first 24 hours.
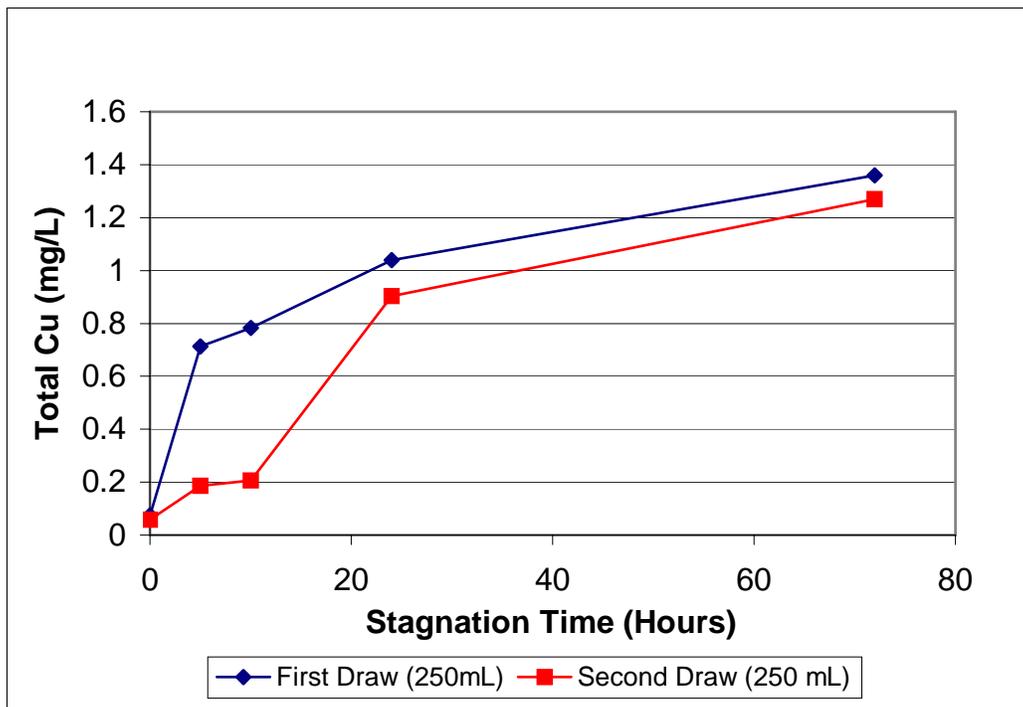
Figure 21. Copper Concentration vs Stagnantion Time
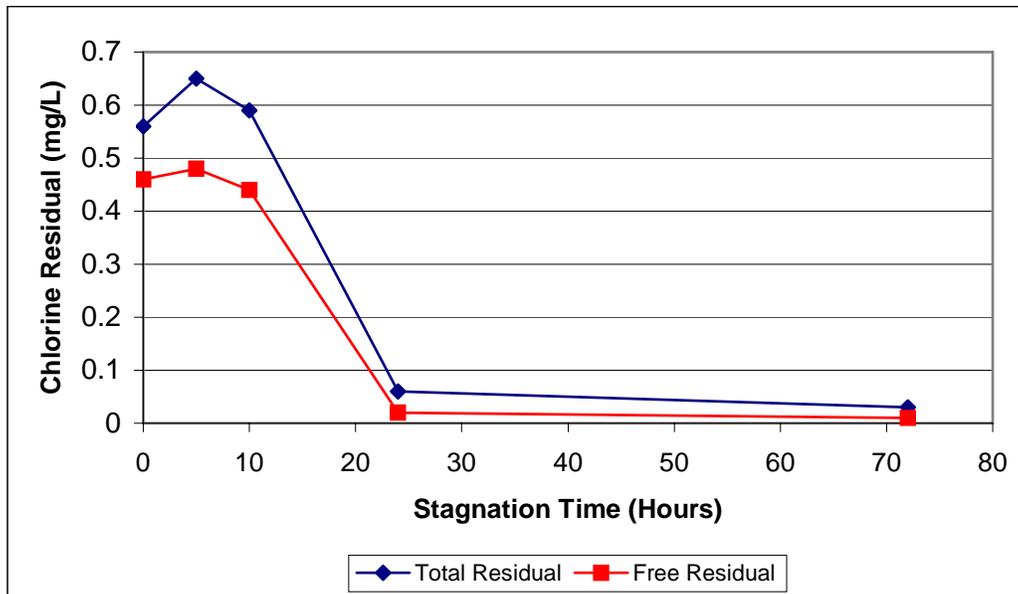
Figure 22. Chlorine Residual vs Stagnation Time

4.1.4. Comparison: Field Test Results and Jar Test Standard Curves.

Before comparing the results of the jar tests and field measurements, a brief

review of the pertinent reactions is in order. The jar tests are intended to duplicate the

reactions which occur in new copper pipe, where $Cu(OH)_2(s)$ is the predominant

component of the solid scale at the pipe surface. As discussed previously, the dissolved

copper concentration in such a system is then driven by the solubility product (K_{sp}) of

$Cu(OH)_2$ in water, through the reaction: $Cu(OH)_2(s) \leftrightarrow Cu^{2+} + 2OH^-$. Copper is

introduced to the sample water in the jar test through the addition of cupric perchlorate,

which adds Cu^{2+} into solution. Therefore, in the absence of orthophosphate, $Cu(OH)_2(s)$

precipitation would be expected in accordance with the cupric hydroxide reaction and

solubility product described above. As orthophosphate is introduced to the system, the

additional reaction, $Cu_3(PO_4)_2 \cdot 2H_2O(s) \leftrightarrow 3Cu^+ + 2PO_4^{3-} + 2H_2O$, is expected, and

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according to the literature (refer to Section 2.4), should result in greater precipitation due to the lower solubility product of the cupric phosphate relative to cupric hydroxide, reducing dissolved copper concentration.

In Figures 23 and 24, the relationship between copper concentration and orthophosphate concentration, as determined from jar tests and field observations, are compared. Field results shown in Figure 23 show copper and orthophosphate measurements after 12 hours stagnation, while Figure 24 indicates measurements taken after flushing.
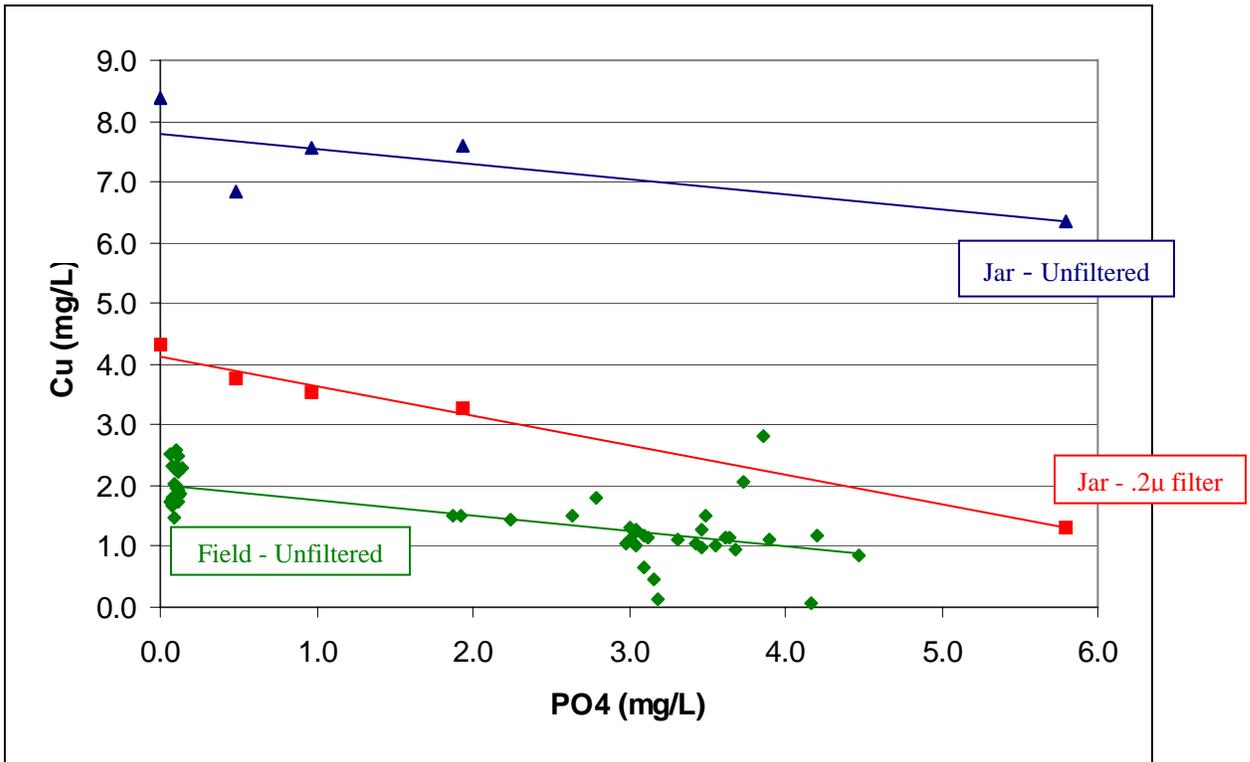
Figure 23. Field (Stagnant) vs Jar Test Results, PO_4 - Cu Concentration
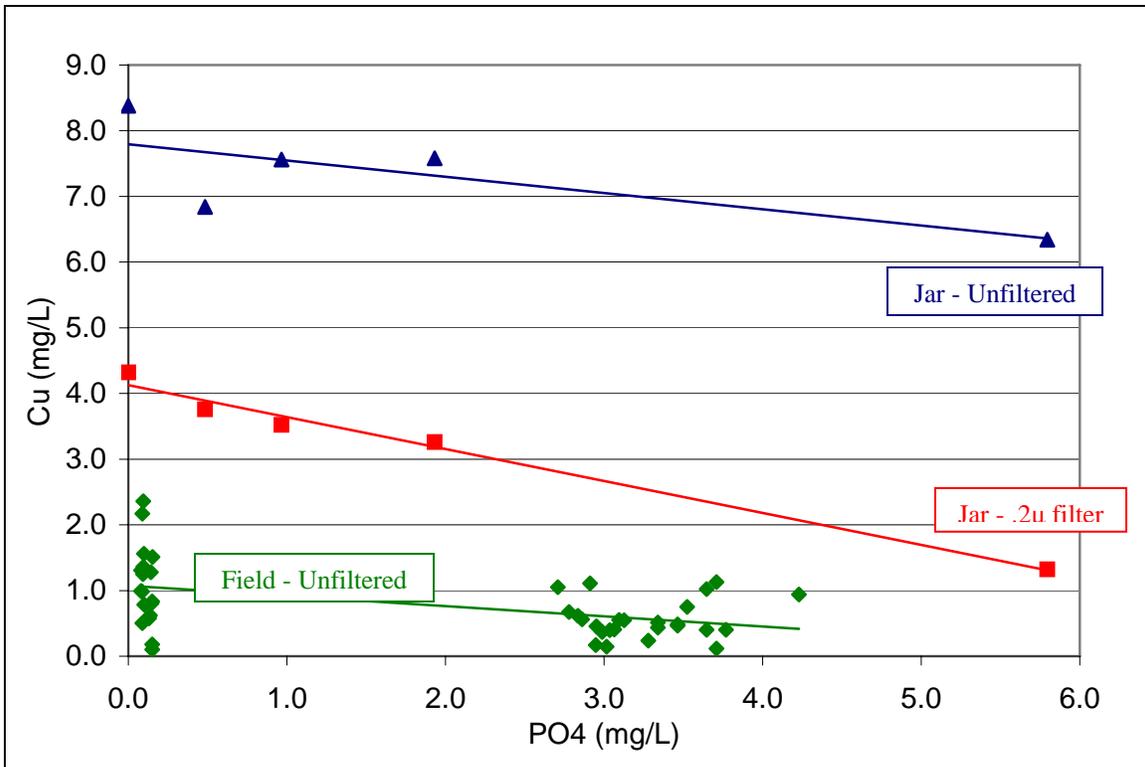
Figure 24. Field (Flushed) vs Jar Test Results, PO_4 - Cu Concentration

A quantitative comparison of the relationship is included in Appendix E, in which linear equations relating Cu-PO_4 concentrations are provided. In both the flushed and stagnant cases, the relationship between orthophosphate and copper concentration follow similar trends; an orthophosphate concentration increase results in a copper concentration decrease. The initial copper levels are considerably higher in the jar test experiments, due to the fact that spiked copper is thoroughly mixed with the sample water. Under these experimental conditions, copper concentrations, when there is no orthophosphate present, are approximately 8 mg/L (unfiltered) or 4 mg/L (0.2 µg filter), compared to the 1 – 2 mg/L concentration observed in the field measurements. (see Figure 21). These values are considerably higher than the theoretical equilibrium levels, 1.0 mg/L at pH 7.5,

(see Appendix B); a discussion of this discrepancy is included in below in section 4.2.3.

However, the effect of orthophosphate addition on copper concentration is similar,

regardless of the initial copper concentration before the orthophosphate was added.   The

following summary table (Table 4) indicates the decrease in total copper concentration

(mg/L) per of 1 mg/L increase in orthophosphate:

Table 4. Decrease in Copper per Unit Increase in Orthophosphate

	Flushed	Stagnant
Field (unfiltered)	0.158	0.253
Jar (unfiltered)	0.258	
Jar 0.2 (ug filter)	0.487	

Note that the effect of orthophosphate addition on copper concentration determined using

filtered jar tests is approximately double that measured in unfiltered tests (both field and

jar tests), suggesting that orthophosphate may more effectively reduce soluble, rather

than particulate, copper. Examining the unfiltered field samples and the unfiltered jar

tests, it can be noted that the 12-hour stagnant field samples compare more favorably to

the jar test results than the flushed sample. Again, this relationship may be due to the fact

that the jar test cell is agitated for 30 minutes, providing a closer approximation of the

conditions, which develop in the field system after 12 hours stagnation.

No meaningful comparison could be made between laboratory and field results

for the soluble copper-pH relationship. Although copper solubility appears to be a clear

function of pH when all other parameters are held constant (refer to figure 4.1, above),

the field measurements taken during this research were conducted in such a narrow pH

range that there was no basis for a comparison.

4.1.5. Field Results: Orthophosphate Effects Due to Time And Distance

The following figures (Figures 25 through 27) display the change in orthophosphate concentration during a twelve-hour stagnation period in each of the three sampling locations of the WPAFB CDC. The first bar at each data point represents orthophosphate concentration due to the injection of orthophosphate during fully flushed operating conditions in late afternoon. After water flow was finished for the day, the sampling faucets were closed (per procedures described in Section 3.3.2.) and no additional orthophosphate was injected into the system. The second bar in each figure represents the orthophosphate concentration from the same sampling location after a twelve-hour stagnation time.
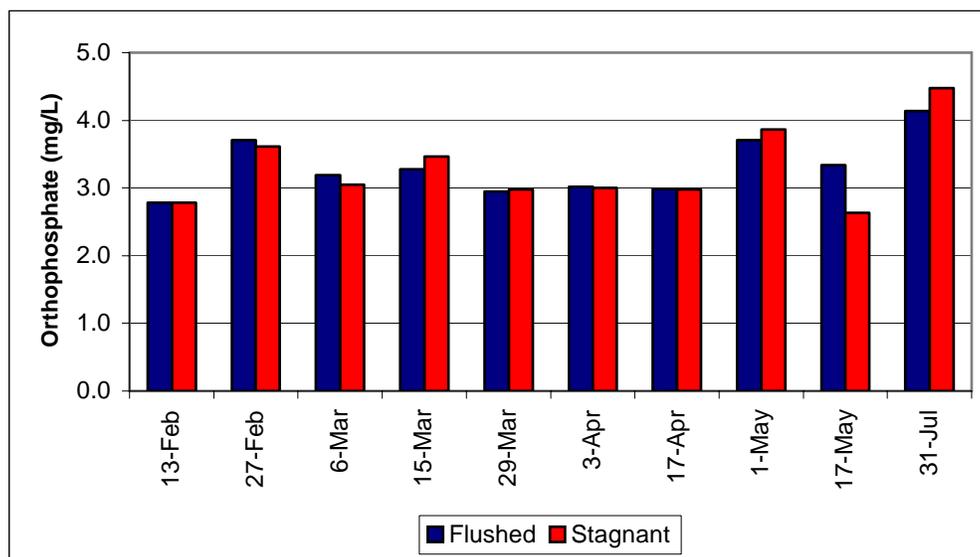
Figure 25. Orthophosphate Change (Rm AP)
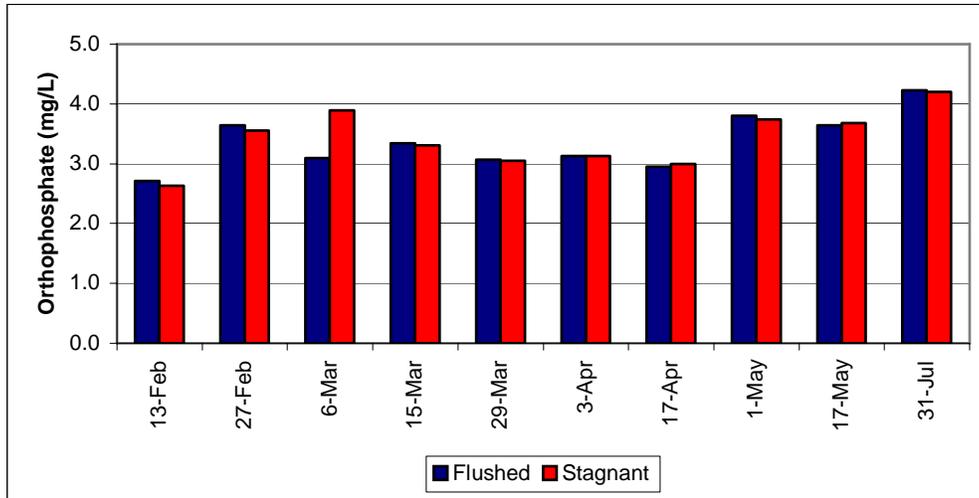
Figure 26. Orthophosphate Change (Rm A6)
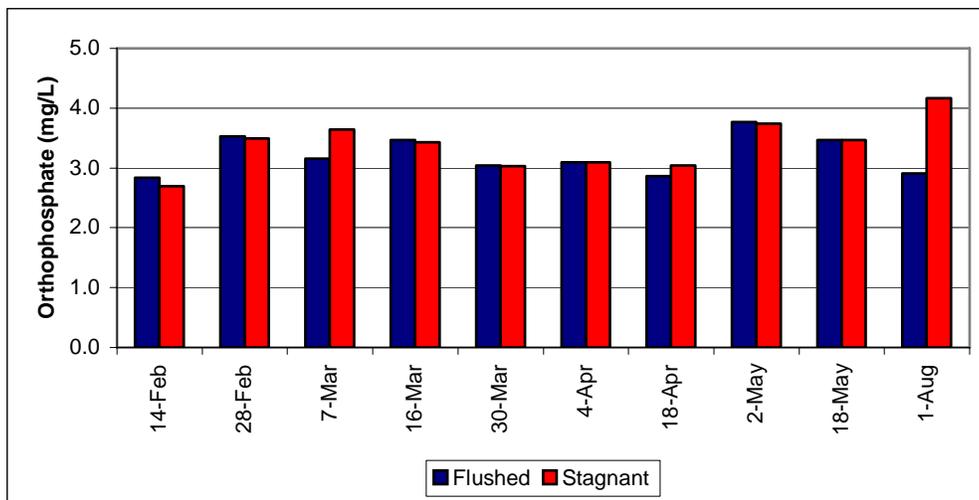
Figure 27. Orthophosphate Change (Rm B14)

There is no clear trend in orthophosphate concentration change over time: the

concentrations are statistically the same before and after the 12 hours stagnation time. In

some cases, the orthophosphate concentration appears to increase after stagnation, even

though no orthophosphate is being added. Based on these observations alone, there is no

evidence that orthophosphate is being consumed by a reaction with copper during the stagnation period: if such a reaction was occurring, a consistent decline in orthophosphate levels would be expected.

In a similar analysis, Figures 28 and 29 compare the orthophosphate concentration in location AP (a few meters downstream of the orthophosphate injection) to the concentration at the far ends of the distribution system (locations A6 and B14, each approximately 70 meters downstream of AP). The comparison is offered for both flushed (Figure 28) and stagnant (Figure 29) measurements.
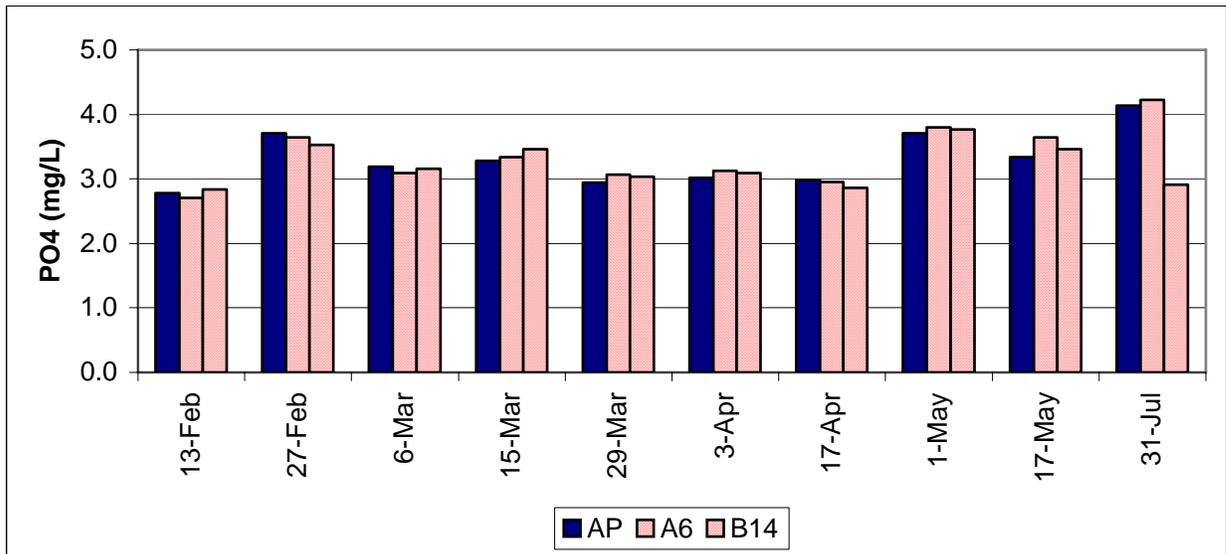
Figure 28. Orthophosphate at Beginning and End of Water Distribution Lines, Flushed
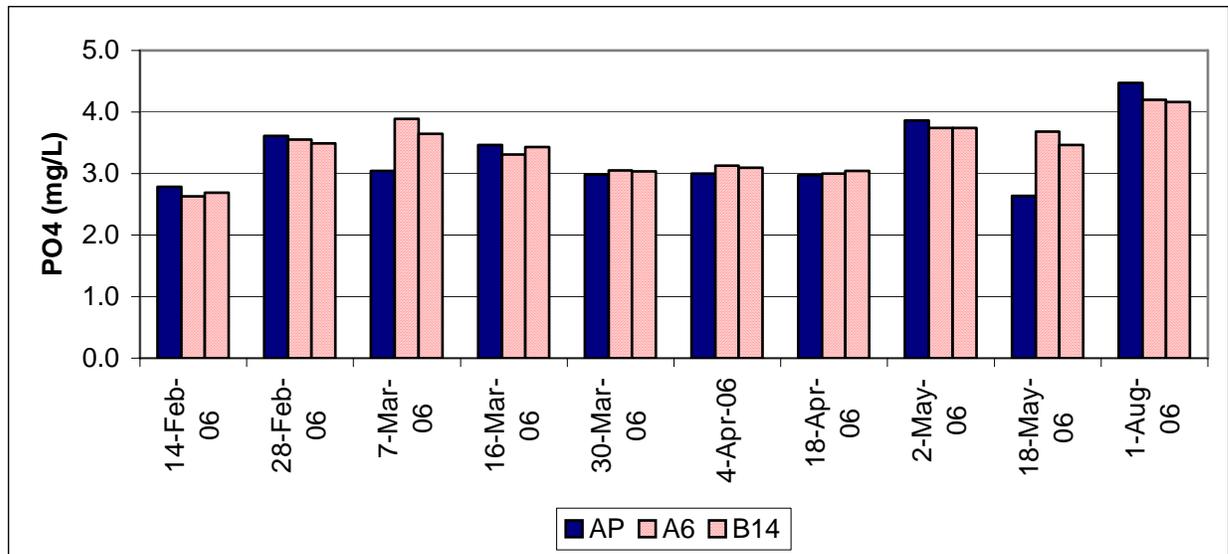
Figure 29. Orthophosphate at Beginning and End of Water Distribution Lines, Stagnant

Once again, there is no clear evidence of a decline in orthophosphate with distance from the orthophosphate injection source. If orthophosphate was being consumed in significant quantities through reactions in the water or along the pipe surface, a consistent decrease in orthophosphate concentrations from location A6 to the terminal locations would be expected.

4.1.6. Solid Species Present Before and After the Orthophosphate Treatment.

Before Treatment

Based on XRD and stereomicroscopic scanning results (compiled in Appendix G), the interior surface prior to the orthophosphate treatment is dominated by elemental copper (77%), carbon, (10%), oxygen (10%), with low phosphorus (1.7%) and other trace elements (percentages given by weight). Dominant solid species include elemental copper and cuprite (CuO). The interior surface is best described as having traces of a particulate film, with isolated pitting spots, evidence of prior corrosion.

After Treatment

Based on XRD and stereomicroscopic scanning results (see Appendix H), the interior surface after the orthophosphate treatment is dominated by elemental copper (65%), carbon, (19%), oxygen (12%), with low phosphorus (1.9%) and other trace elements. Dominant solid species still include elemental copper and cuprite. The interior surface appears to have a slightly more uniform film than seen on the pretreatment surface.

4.2. Discussion

4.2.1. Is Orthophosphate Effective For Reducing Dissolved Copper?

During the course of this research, six cases were examined: three sampling locations (rooms AP, A6, and B14 of building 20630), both after flushing and following stagnation. In five out of six cases, the addition of orthophosphate led to a statistically significant reduction in copper levels (at a 95 percent confidence level), with mean copper concentrations below the 1.3 mg/L action level. A summary of the six cases is tabulated below:

Table 5. Statistical Analysis of Change in Mean Copper Concentration

Location	Time	Mean [Cu] Before PO_4	Standard Deviation	Mean [Cu] After PO_4	Standard Deviation	95% Confident That Means Are Statistically Lowered?		
		(mg/L)		(mg/L)		95% 2-tailed Student's t	Calculated t Statistic	Significant? (Calc t > 95% t)
AP	Flushed	0.567	0.407	0.430	0.307	2.15	0.74	No
AP	Stagnant	1.825	0.343	1.284	0.596	2.11	2.51	Yes
A6	Flushed	1.088	0.233	0.624	0.273	2.13	4.23	Yes
A6	Stagnant	1.886	0.171	1.194	0.337	2.10	6.04	Yes
B14	Flushed	0.988	0.200	0.593	0.210	2.13	3.97	Yes
B14	Stagnant	1.747	0.292	1.020	0.401	2.11	4.56	Yes

In the only case where no significant decrease occurs, it should be noted that the initial

copper concentration of 0.567 mg/L is well below the copper action level—and below the

copper concentrations at the other building locations—prior to the orthophosphate

treatment. This is likely due to the sampling location's placement: at only about six

linear meters from the building's water service entrance, the water has not been in contact

with the building's copper lines long enough to develop a high copper concentration.

Also note that the exceptional case occurs during a flushed sample measurement;

as expected, the stagnant sample at the same location yields a higher initial copper

concentration, and subsequently, a more significant reduction after orthophosphate

treatment. The statistical analysis and calculations are included in Appendix F.

Therefore, assuming that all other influent water quality parameters were

maintained constant throughout the experimental period, there appears to be statistically

significant evidence that orthophosphate reduces copper concentration in high alkalinity

drinking water systems. To examine the other water quality parameters before and after

the addition of orthophosphate, the following summary table is provided to identify any

changes in pH, temperature, dissolved oxygen, chlorine residual, and total alkalinity:

Table 6. Water Quality Characteristics Before and After Orthophosphate

	pH	Temp (deg C)	DO (mg/L)	chlorine-free (mg/L)	chlorine-total (mg/L)	alkalinity (mg/L as CaCo3)
mean (before PO$_4$)	7.53	21.03	7.48	0.13	0.20	271.92
mean (after PO$_4$)	7.37	20.40	8.08	0.25	0.42	272.83
95% confidence "t"	2.01	2.02	2.02	2.12	2.05	2.06
test t	4.92	1.70	3.92	1.45	1.96	0.10
significant difference?	YES	NO	YES	NO	NO	NO

There were no statistically significant changes in four of the parameters: alkalinity, temperature, free and total chlorine. The measurements of flushed samples indicate that the mean alkalinity remained high (approximately 272 mg/L as $CaCO_3$) throughout the sampling period. The mean free and total chlorine residuals ranged between 0.13 – 0.25, and 0.20 – 0.42 mg/L, respectively, but did not change significantly with the introduction of orthophosphate. The mean water temperature remained statistically constant throughout the sampling period, at approximately 21°C.

There was a statistically significant change in two parameters: pH and dissolved oxygen. The decrease in pH level is likely due to fluctuations in the source water quality, rather than any effect of the added orthophosphate. Source water quality reports in Appendix A indicate that Area B water's pH fluctuated in a range between 7.2 – 7.5 during the sampling period. Furthermore, based on the pH-copper solubility relationship established in Figure 10, such a decrease in pH would typically lead to increased copper solubility. Therefore, the observed decrease in copper solubility, despite the pH decrease, provides further evidence to support orthophosphate's effectiveness as an inhibitor of copper solubility.

Finally, while it is unknown whether the increase in dissolved oxygen is a result of any source water fluctuations, it is possible that the oxygen increase results from the addition of orthophosphate in the CDC system. According to the literature, an increase in dissolved oxygen is an expected effect: Dartmann et al. (2004) propose that "dosing of orthophosphate can lower the content of copper in water by reducing the oxygen consumption." Therefore, while the oxygen level increase cannot conclusively be

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attributed to either the source water or the orthophosphate's impact, the change does not contradict that observed in previous studies.

The system costs to date include a $15,000 investment for design and installation, along with a $1,200 monthly maintenance and operation expense. Assuming a ten-year capitalization for the system, this equates to a $15,900 annual expense. As a point treatment for a single facility, this represents a considerable expense. Although the effectiveness of the system in reducing dissolved copper has been demonstrated in this research, the cost effectiveness of this treatment as a long-term solution is not clear. While beyond the scope of this investigation, the option of orthophosphate source treatment at the production wells (vice point treatment at the facilities) may be a more economic alternative, especially if additional facilities are found to contain elevated copper concentrations in their drinking water systems.

4.2.2. What Reactions Are Occurring?

Water Quality Data Indicators

Water quality measurements after the addition of orthophosphate indicated a slight decrease in pH (likely due to source water fluctuation), a slight increase in dissolved oxygen, consistent levels of chlorine residual and alkalinity, and a consistent decrease in copper concentration after a 12 hour stagnation period. These measurements are consistent with a transition from $Cu(OH)_2$ (s) to $Cu_3(PO_4)_2$ (s) on the interior pipe surface, as predicted in the literature (Edwards et al., 2005). The decrease in copper's observed concentration corresponds to the decrease in the equilibrium solubility of the respective solids due to the solubility product of the two species ($\log K_{s0}$ (cupric

hydroxide) = 8.89; log K_{s0} (cupric phosphate) = -36.76 (Schock et al., 1995)) when measured at the same alkalinity and same (or lower) pH levels.

Stagnation Time and Distance Indicators

No significant change in orthophosphate concentrations was observed between measurements at the tap near the location where orthophosphate was added, and taps 70 meters downstream (see Figure 28). The steady levels of orthophosphate throughout the facility's drinking water distribution system suggest that the orthophosphate is not being consumed while in the building's distribution system. In terms of stagnation time, the orthophosphate concentration does not appear to decrease significantly during a 12-hour stagnation period (Figures 25 through 27), again an observation that appears to indicate that orthophosphate is not being consumed in the building's distribution system. An interesting observation is the near-immediate impact of the orthophosphate treatment: copper concentration was reduced by over one-third of its pre-treatment levels within the first week of orthophosphate addition in February 2006 (the drop is clearly indicated in Figures 18 and 19). This phenomenon, along with the apparent non-reactivity of the orthophosphate over distance and short-term stagnation time, may suggest a mechanism for the copper reduction. The creation of a passivating film, or development of a lower-solubility solid on the interior pipe walls may have occurred immediately upon introduction of the orthophosphate. It is unknown whether the continued injection of orthophosphate is required to replenish the film/solids due to other reactions or degradation, as there is little evidence of orthophosphate consumption within the treated system. Measurements of the water quality parameters following a brief or sustained suspension of the orthophosphate treatment might provide valuable insight.

Solid Analysis Indicators

A comparison between the pre- and post-treatment pipe surface may be drawn

based on the visual, compositional, and spectrographic data in Appendices G and H.

Visual inspection indicates that the solid film appears to be slightly more uniform in its

coverage on the surface of the post-treatment pipe. A comparison of pre- and post-

treatment elemental composition indicates a decrease in elemental copper and increases

to carbon, oxygen and phosphorus. However, XRD analysis of both pre- and post-

treatment pipe samples indicates that copper metal and cuprite are the dominant species

in both cases. Taken together, these solids indicators do not provide conclusive evidence

of any specific reactions that occurred after the introduction of orthophosphate.

4.2.3. How Do Results Compare With Equilibrium Models?

In general, the values calculated by the cupric hydroxide model and VMINTEQ

are relatively good predictors of laboratory or field measurements. Figure 30, which

compares the cupric hydroxide and VMINTEQ model predictions to jar test

measurements for the copper-pH relationship, indicates that copper control cannot

reasonably be achieved at a high alkalinity through pH reduction alone: both models and

lab results require a pH greater than 8.5 to reduce copper below 1.3 mg/L. Note that the

jar test does not rise exponentially as pH decreases toward 6.5, as predicted by the

equilibrium models. This limitation is simply due to the fact that the jar test was

performed after spiking the sample water with a 15 mg/L copper solution: this dose set an

upper limit on maximum copper concentration, regardless of pH.
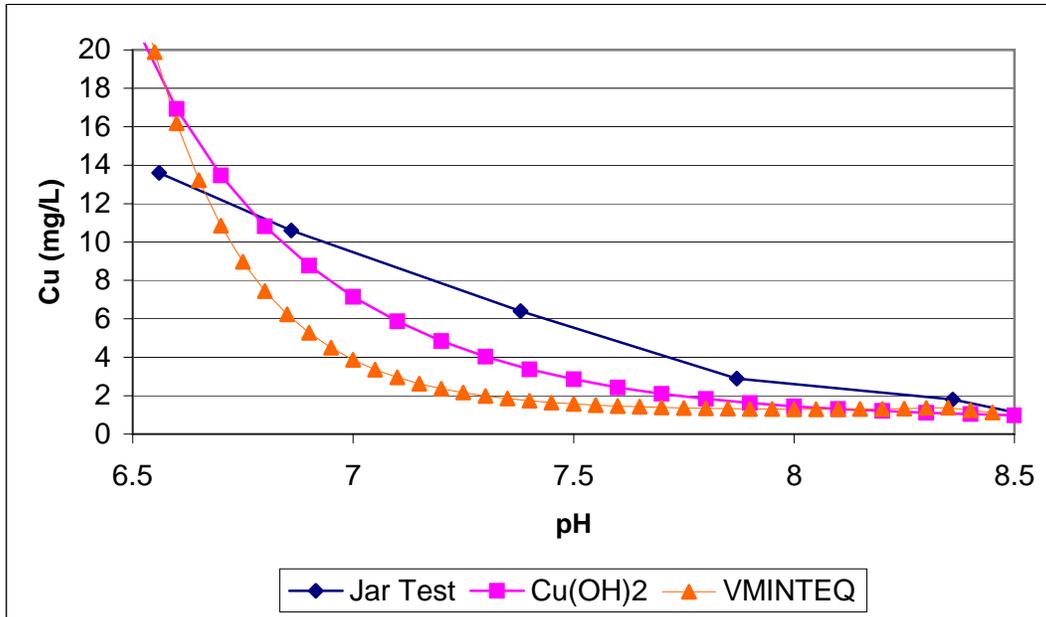
Figure 30. Model Predictions vs Jar Test, Copper – pH

Similarly, Figure 31 provides a comparison between both model predictions and

jar test measurements for the copper – orthophosphate relationship.
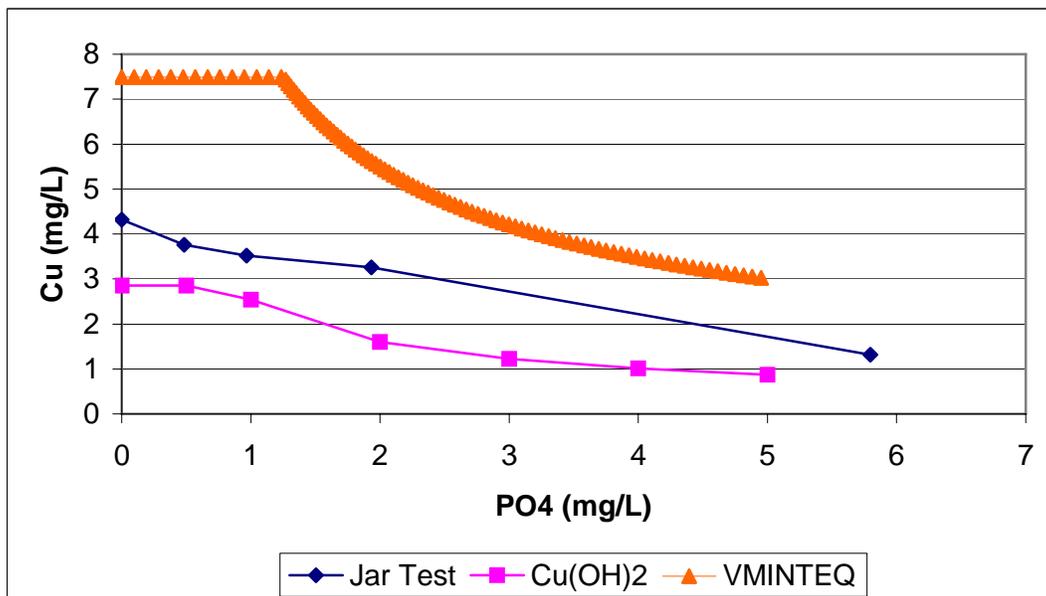

Figure 31. Model Predictions vs Jar Test, Copper – Orthophosphate

Note that while all three relationships follow the same trend, there is a greater disparity between the models' predictions and the jar test results than were observed in the copper-pH relationships shown in Figure 30. While the cupric hydroxide model slightly under-predicts the observed jar test values for copper concentration, the discrepancy may be due to small levels of solid copper precipitate that passed through the 2.0 and 0.2 μm filter and were then measured in the ICP as total copper. The model's predictions are based purely on dissolved copper levels, and would therefore be slightly lower than the observed values. While the VMINTEQ predictions are higher than both the cupric hydroxide model and the jar test results, this difference is due to the higher solubility constants used in the VMINTEQ model. The thermodynamic constants used in the cupric hydroxide model are empirical values based on a process of continual updates from laboratory and field measurements, and appear to provide a more accurate prediction of equilibrium solubility than VMINTEQ. However, when the VMINTEQ program is run using the cupric hydroxide constants, its revised predictions are much closer to the cupric hydroxide model results.

Figure 32 presents a comparison of model predictions and field measurements for the copper – orthophosphate relationship. Like Figure 31, there is a similar trend for each of the three relationships. As discussed above, VMINTEQ slightly over-predicts the field and the cupric hydroxide model results due to the high solubility constants used in that model. The cupric hydroxide model over-predicts copper concentration in the absence of orthophosphate, but after the orthophosphate dosage increases above 2 mg/L, the model tracks closer to the linear trend line derived from the field measurements. Due to a few extreme values, the standard deviation of the field measurement's linear trend line is

0.53. The discrepancy at low orthophosphate levels may simply be a result of the copper

in the system failing to equilibrate after only 12 hours. Measurements taken 48 to 72

hours later would likely correspond more closely to the model's predicted equilibrium

values.
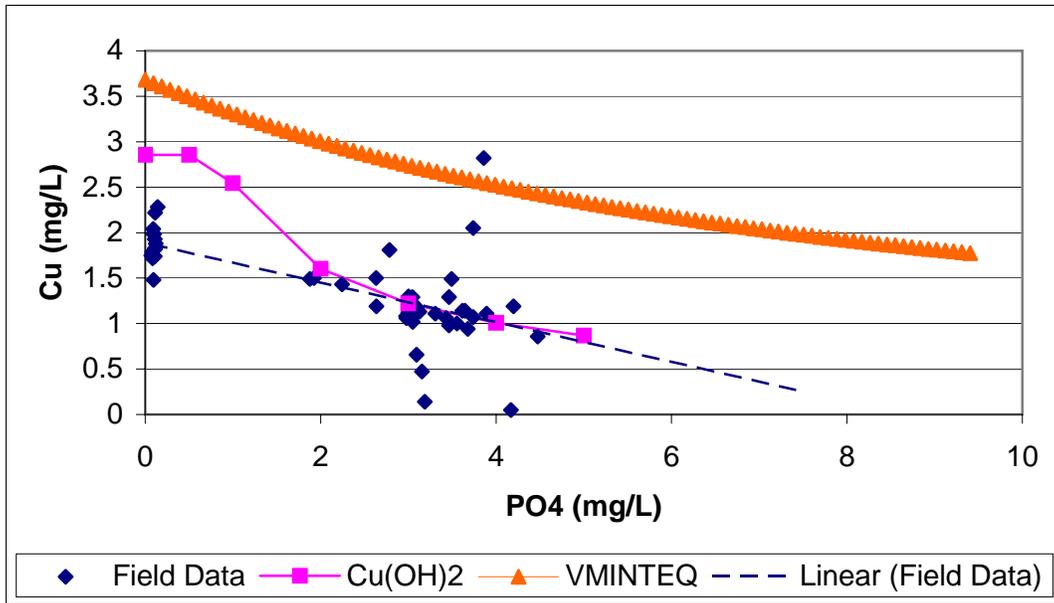
Figure 32.   Model Predictions vs Jar Test, Copper – Orthophosphate

V. Conclusions And Recommendations

5.1. Conclusions

5.1.1. Orthophosphate Effectiveness.

Orthophosphate treatment appears to be an effective method for dissolved copper reduction in high-alkalinity water systems. High-alkalinity water sources present a challenge to water suppliers due to the substantial increase in dissolved copper that is observed to occur in the presence of high carbonate concentrations. Orthophosphate has proved to be an effective solution to reduce copper levels when high alkalinity and hardness prevent pH adjustment. This research has demonstrated that orthophosphate can provide effective and sustained reduction in copper concentrations to below the LCR action level of 1.3 mg/L in water with alkalinity as high as 280 mg/L.

5.1.2. Recommended Dosage For Orthophosphate Treatment.

For similar waters (pH = 7.5, alkalinity = 280 mg/L), a dose of 3 to 4 mg/L orthophosphate is recommended to ensure adequate protection within a facility's drinking water system. This level is based on both theoretical calculations (using the $Cu(OH)_2$ model) and field observations from this research. Although smaller orthophosphate doses (1.5 to 2.5 mg/L) had a measurable effect on the observed copper concentration, sustained copper levels below the LCR action level were not achieved until the 3 mg/L dosage was implemented.

5.1.3. Orthophosphate Treatment Timeframe.

Orthophosphate injection provides a fast-acting treatment. Significant reduction in copper levels was observed within the first week of orthophosphate addition. Following this initial observation, copper levels remained consistently lower so long as orthophosphate additions were maintained. However, orthophosphate's effectiveness decreases as stagnation time increases, until a maximum copper concentration equilibrates in the system.

5.1.4. Reactions in System.

The increase in elemental phosphorus and oxygen, along with the reduced solid copper solubility, suggest the formation of a phosphate solid, although XRD analysis does not confirm the presence of those solids. The insignificant reduction in orthophosphate levels during 12 hours of stagnation and 70 meters of flow do not indicate the steady consumption of orthophosphate in the water system. Given these observations and the rapid decrease of copper solubility during the first week of orthophosphate treatment, it is possible that the initial orthophosphate doses quickly formed a new phosphate film or solid scale; subsequent orthophosphate consumption is relatively low, and limited to maintenance of that scale.

5.1.5. Modeling.

Chemical equilibrium models such as VMINTEQ or the USEPA cupric hydroxide program are useful tools for predicting the effect of orthophosphate on copper concentration. So long as basic water quality data are available, these models use their thermodynamic databases to calculate the expected concentrations of all species. This research has confirmed that model predictions reasonably approximate field

measurements, demonstrating that these models provide a low-cost and efficient starting point for developing water treatment strategies. The cupric hydroxide model allows the user a greater degree of control over the species to be isolated in a system's reactions, but is difficult to operate. VMINTEQ offers an easier user interface for basic system calculations, but requires additional work if the user wishes to isolate specific reactions or modify thermodynamic data.

5.2. Recommendations For Additional Research

1. Investigate the short- and long-term effects of stopping orthophosphate addition upon dissolved concentrations and the solid film.

2. Repeat the measurements performed in this study under laboratory conditions, using a section of pipe from the WPAFB CDC. In the laboratory, the variables in this research, such as pH, orthophosphate concentration, and stagnation time, could be controlled. Use the results of the controlled study to validate the field observations from this research.

3. Perform continued measurements, including surface analyses, over the next several years to determine if orthophosphate treatment is preventing natural scale buildup in the WPAFB CDC's water lines. A baseline for comparison would be the natural scale that was observed in an earlier study in a range of facilities of various ages at WPAFB (Turek, 2006).

4. Cost analysis. Conduct an analysis to determine the cost and benefits of "point" treatment for copper reduction at individual buildings (as described in this research) compared to source treatment at a water treatment facility. Such an analysis should

consider the potential need for wastewater treatment to manage phosphates that may increase in wastewater as a result of adding orthophosphate at the water source.

5. Additional modeling applications. Using the USEPA $Cu(OH)_2$ model as a baseline, develop an updated model with a more user-friendly interface. Such a modification would combine the ease of use currently provided by VMINTEQ with the level of control currently provided by the $Cu(OH)_2$ model.   Apply the model to simulate results observed in the studies recommended above.

6. Investigate copper levels at 0600 hrs Monday mornings to determine typical concentrations after 48+ hours of stagnation time. If the levels are consistently high, evaluate two options: 1) one-time flushing on Monday mornings to eliminate the long-stagnant water; or 2) increased orthophosphate injection rate to a dosage to that overcomes the Monday-morning levels. Option two would avoid the requirement for flushing (and the possibility that flushing is not performed correctly), but would consume much more orthophosphate during the week than the current 3.0 mg/L level required to achieve 1.3 mg/L copper concentrations Tuesday through Friday.

Appendix A: Water Quality Plant Data

Figures 33 and 34 provide historic water quality data covering the research period (Sep 05 through Jul 06). The data is based on the 88 ABW Environmental Management office's log of Plant Distribution Monthly Operations Reports.
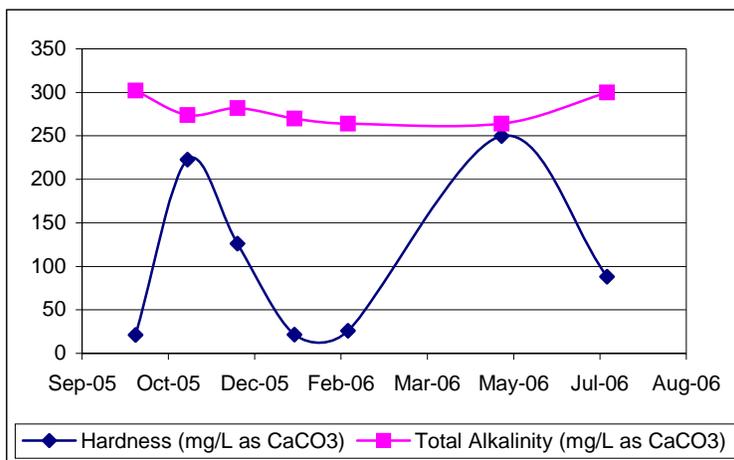

Figure 33. Hardness and Alkalinity Data (Plant Values)
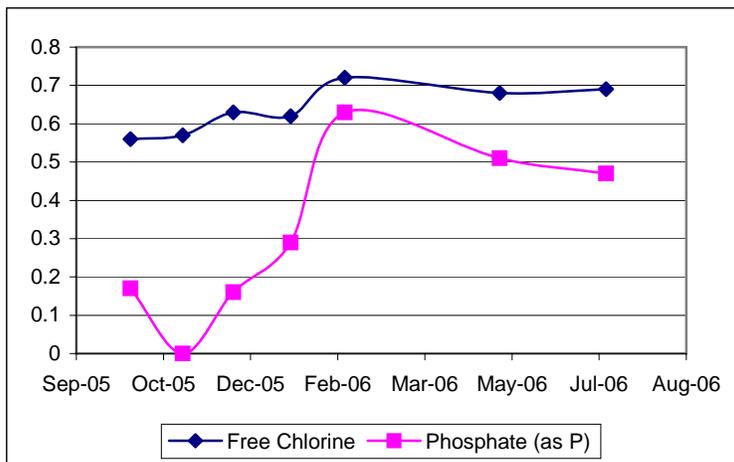
Figure 34. Chlorine and Phosphate Data (Distribution System)

Appendix B: Simplified Calculation For Equilibrium Dissolved Copper Prior To Orthophosphate Treatment

The concentration of total dissolved copper in equilibrium with solid $Cu(OH)_2$ is calculated below as 1.1mg/L. The calculation assumes a simplified system in which only $Cu(OH)_2$ (s) and associated dissolved Cu^{2+} hydroxide species are present in distilled water; alkalinity or carbonate species are not considered. Note that the values of the solubility product (K_{s0}) and stability constants (*B) are based on those reported by Schock et al (1995). Using the Excel Solver algorithm, the total dissolved copper concentration was iteratively adjusted until the activity quotient (Q_0) matched the solubility product for the given pH value. This point represents the maximum theoretical level of dissolved copper at that pH.

Note that these calculations are performed in a simplified system in which $Cu(OH)_2$ (s) and the Cu^{2+} hydroxide species are considered in isolation: no consideration for alkalinity or carbonate species are included in the calculations. Therefore, when comparing these results to the model output values, the model simulations should be performed in the absence of carbonates to allow a meaningful comparison. (Refer to Figure 3.7. for further discussion).

Finally, it should be noted that the pH selected for these calculations (7.5) is based on the typical level observed in the field. In this simplified system, charge balance would drive the pH to a level of 9.2 if only the species identified in Worksheet 1 were present; at that point, the copper concentration would be reduced to an insignificant level. A pH

near 7.5 could be sustained through the addition of a weak acid/base pair to serve as a

buffer in the neutral range.

The calculations (performed in MS Excel) are provided below.

1. Water Parameters:		pH	7.5	1E-14		
		$\{H^+\}$	3.16E-08			
		$\{OH^-\}$	3.16E-07			

2. Solubility Product (K_{s0}) $Cu(OH)_2$:		log $*K_{s0}$	$*K_{s0}$	$K_{s0} = *K_{s0} \times K_w^n$	K_{s0}	log K_{s0}
(Schock, 1995: Table 2):		**8.89**	7.76E+08		7.76E-20	-19.11

3. Mass Balance:

(Benjamin, 2002: Eqn 8.40): $TOTCu = \{Cu^{2+}\}(1+[sum(B_{OH}\{OH^-\})])$

	n OH^-	Reaction	***log B**	*B
(Schock, 1995: Table 2):	1	$Cu^{2+} + OH^- <> Cu(OH)^+$	**-7.98**	1.05E-08
	2	$Cu^{2+} + 2OH^- <> Cu(OH)_2$	**-13.68**	2.09E-14
	3	$Cu^{2+} + 3OH^- <> Cu(OH)_3^-$	**-26.9**	1.26E-27
	4	$Cu^{2+} + 4OH^- <> Cu(OH)_4^{2-}$	**-39.6**	2.51E-40

$B = *B / K_w^n$	B	log B	$\{OH^-\}^n$	$B\{OH^-\}^n$
	1.05E+06	6.02	3.162E-07	3.31E-01
	2.09E+14	14.32	1E-13	2.09E+01
	1.26E+15	15.1	3.162E-20	3.98E-05
	2.51E+16	16.4	1E-26	2.51E-10
				2.12E+01

$\{Cu^{2+}\} = TOTCu / (1+[sum(B_{OH}\{OH^-\})])$

$\{Cu^{2+}\}$			$\{Cu^{2+}\}$		
(M)	7.76E-07		(mg/L)	4.93E-02	

4. Solubility Calculations:

Activity Quotient (Q_0): $Q_0 = \{Cu^{2+}\}\{OH^-\}^2$

			log
	Q_0	7.76E-20	-19.11000
(From above):	K_{s0}	7.76E-20	-19.11000
		5.232E-26	0.00000

(Precipitation or Dissolution?): Will Precipitate

(Equilibrium Summary): $TOTCu = \{Cu^{2+}\}(1+[sum(B_{OH}\{OH^-\})])$

TOTCu			TOTCu		
(mg/L)	1.0955		(M)	1.73E-05	

Appendix C: Soluble Copper vs pH Jar Tests Results

The raw results of the copper vs pH jar test procedure are provided in Table 7.   A

linear regression of this data is illustrated in Figure 35.

Table 7. Jar Test Results, Copper vs pH

| pH	Cu (mg/L)
6.56	13.6
6.86	10.6
7.38	6.4
7.87	2.9
8.36	1.8
8.55	0.9
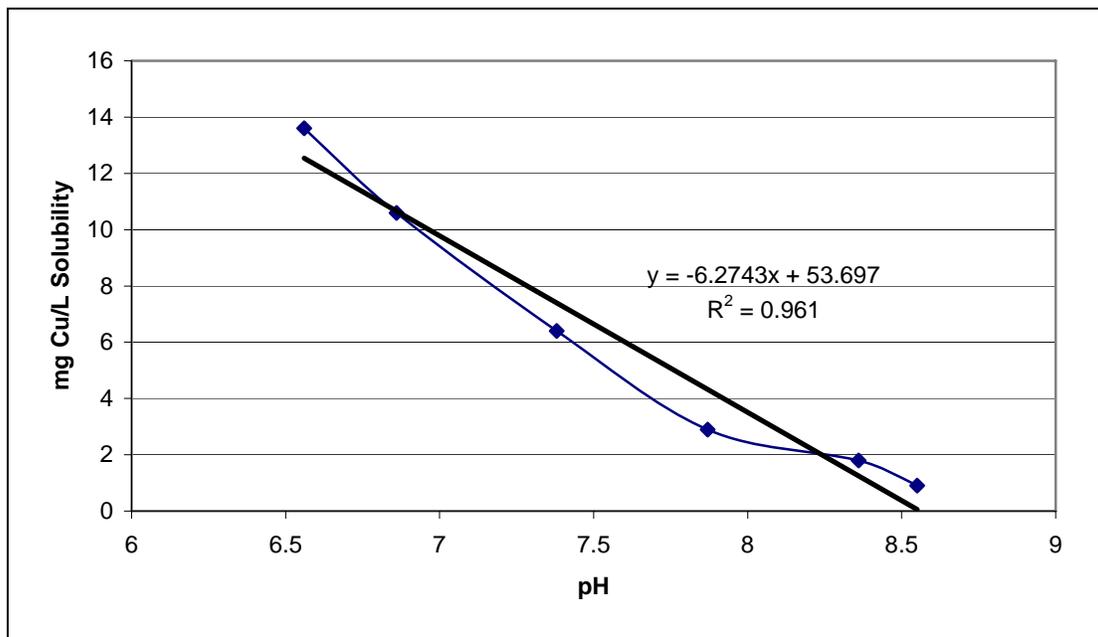
Figure 35. Copper vs pH Linear Equations

Appendix D: Soluble Copper vs Orthophosphate Concentration

The raw results of the copper vs orthophosphate jar test procedure are provided in

Table 8.   A linear regression of this data is illustrated in Figure 36.

Table 8. Jar Test Results, Copper vs Orthophosphate

| Sample	pH	PO4 Background d (mg/L)	PO4 Added (mL)	**PO4 Added (mg/L)**	PO4 Total (Predicted) (mg/L)	PO4 Actual (Unfiltered) (mg/L)	PO4 Final (Filtered) (mg/L)	Cu Background (mg/L)	Cu Added (mL)	Cu Added (mg/L)	Cu Total (Predicted) (mg/L)	Cu Actual (Unfiltered) (mg/L)	**Cu Final (Filtered) (mg/L)**
0	7.44	0.63	0.00	**0.00**	0.63	0.63	0.63	2.76	4.50	6.03	8.79	8.38	**4.32**
1	7.51	0.63	0.35	**0.48**	1.11	1.02	2.52	2.76	4.50	6.03	8.79	6.84	**3.76**
2	7.59	0.63	0.70	**0.97**	1.60	1.47	1.27	2.76	4.50	6.03	8.79	7.56	**3.52**
3	7.51	0.63	1.40	**1.93**	2.56	2.14	0.51	2.76	4.50	6.03	8.79	7.58	**3.26**
4	7.52	1.28	4.20	**5.80**	7.08	6.17	1.99	1.72	4.50	6.03	7.75	6.34	**1.32**
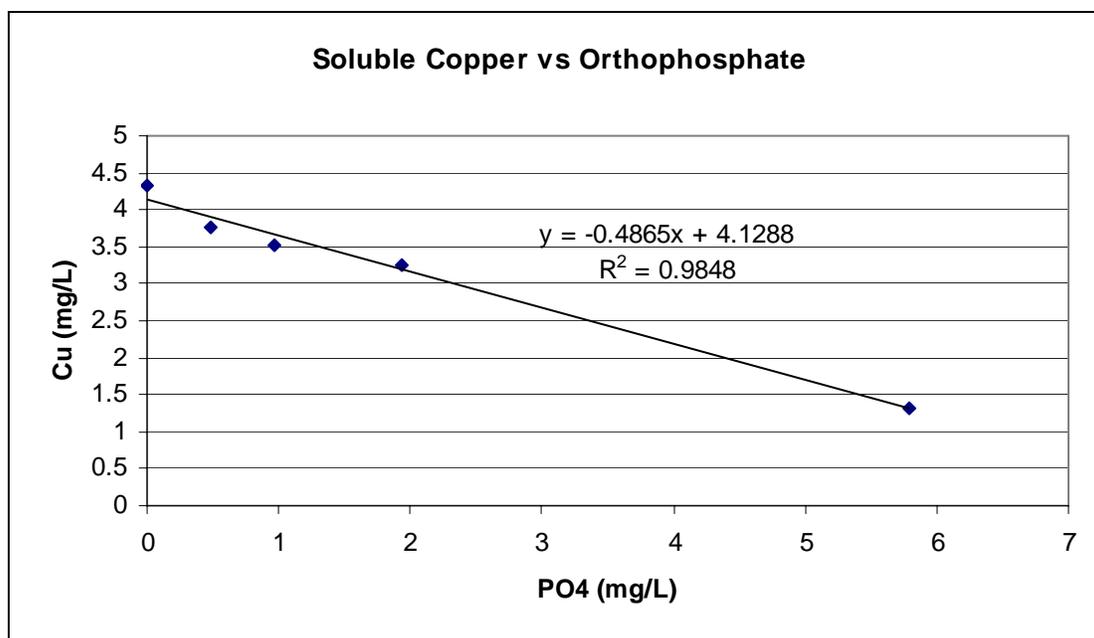
Figure 36. Copper vs Orthophosphate Linear Equations

Appendix E: Field Results vs Jar Test Comparison

Figures 37 and 38 provide a comparison between the results of jar test measurements and field data. The charts plot copper concentration as a function of orthophosphate dosage. The linear equations representing the three cases are provided on each chart.
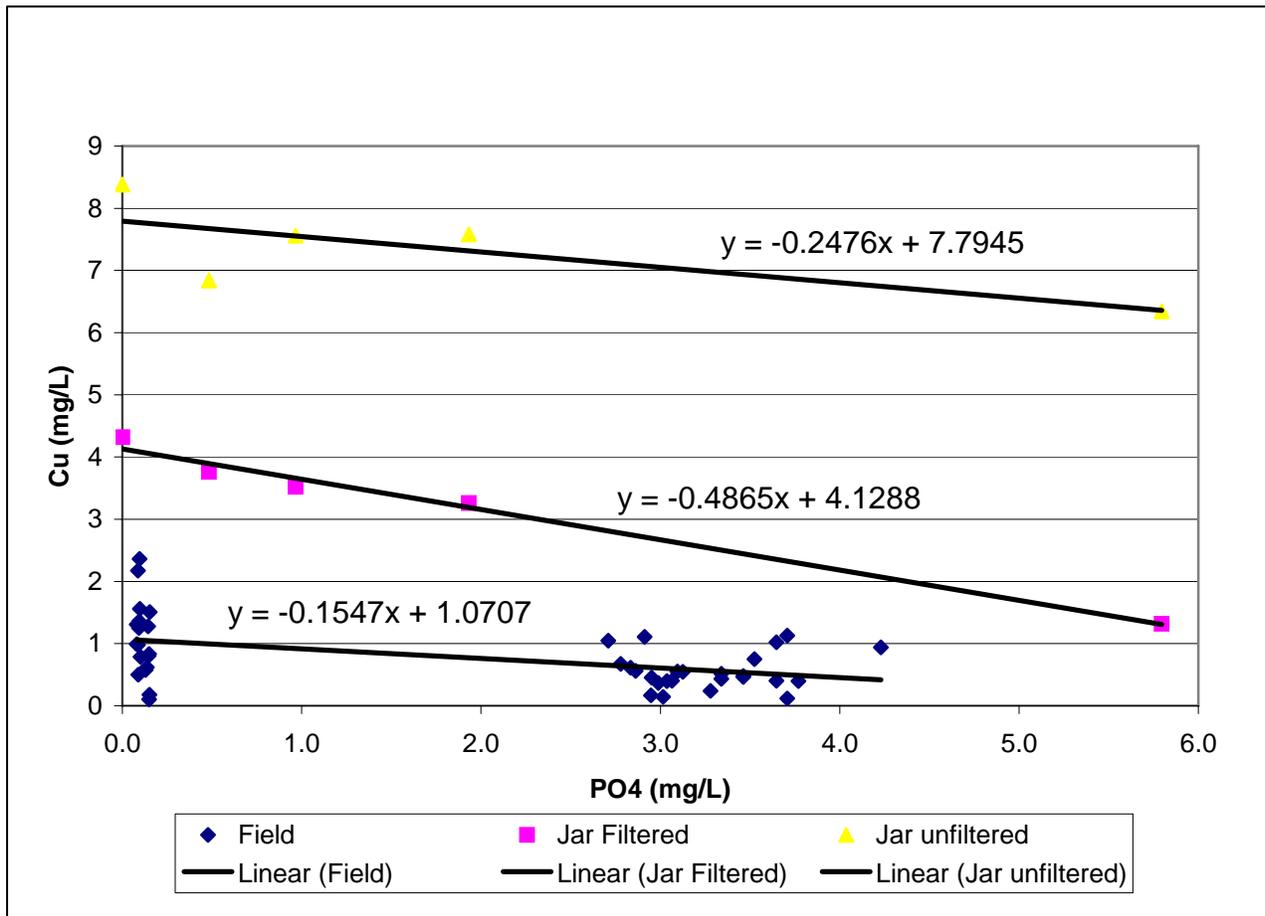

Figure 37. Flushed Field vs Jar Test, Linear Equations
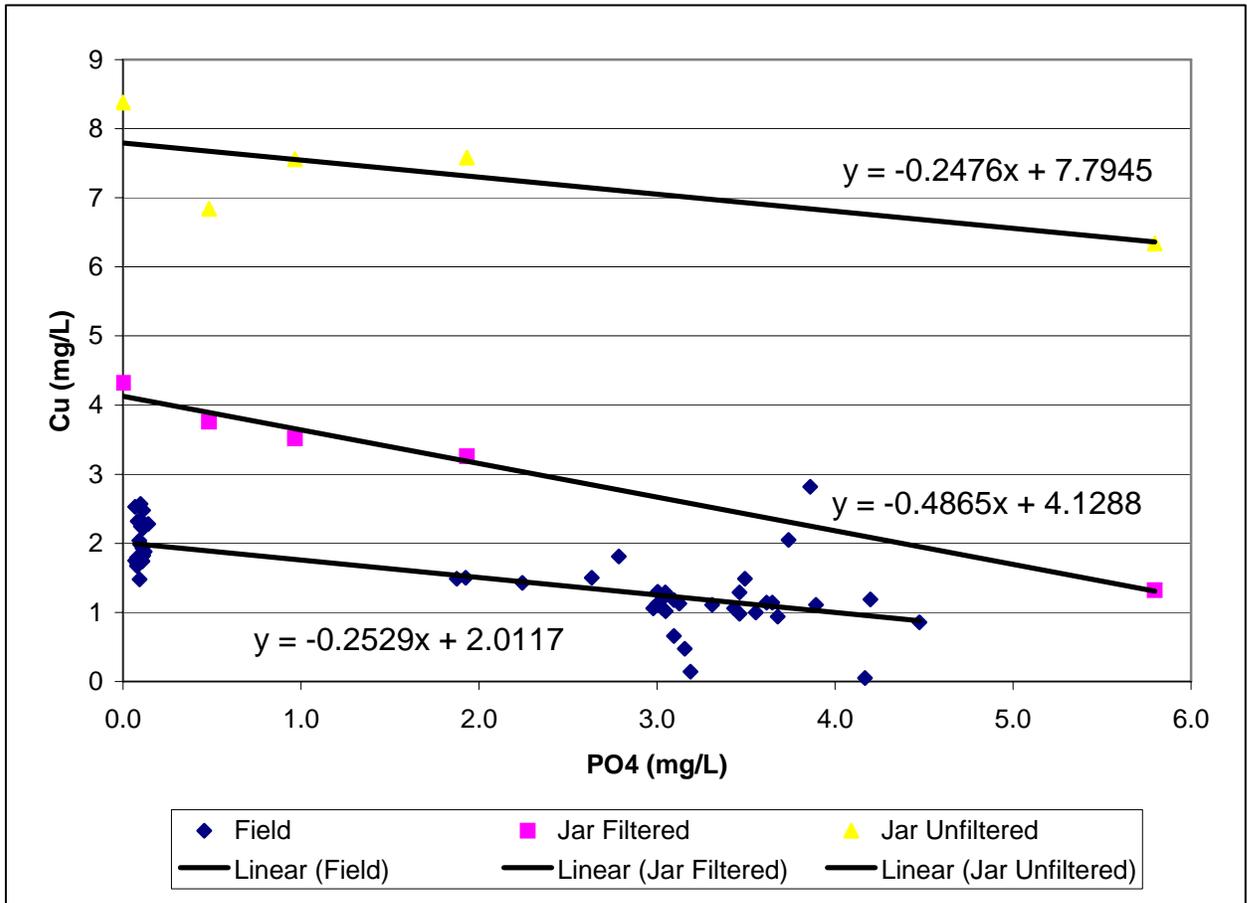
Figure 38. Stagnant Field vs Jar Test, Linear Equations

Appendix F: Statistical Analysis of Change in Mean Copper Concentration

For each of the six cases the copper concentrations were tabulated for all measurements taken before the orthophosphate treatment (typically eight samples between October and December 2005, "n_1") and all measurements taken after the treatment started (typically twelve samples between February and August 2006, "n_2"). For both the "before" and "after" series of measurements, a mean concentration, standard deviation, and sample variance were computed. The rejection region for a 95% confidence interval was defined from a Student's t table using $t_{\alpha/2} = 0.025$, using

$$\text{degrees of freedom } (\nu) = \frac{\left(\left(\frac{s_1^2}{n_1}\right)+\left(\frac{s_2^2}{n_2}\right)\right)^2}{\frac{\left(\frac{s_1^2}{n_1}\right)^2}{n_1-1}+\frac{\left(\frac{s_2^2}{n_2}\right)^2}{n_2-1}} \;,$$

where s = sample standard deviation,

n = sample size for the "before" ($_1$) and "after" ($_2$) samples.

The test statistic for each case was calculated by the equation:

$$t = \left(\bar{X}_1 - \bar{X}_2\right) / \sqrt{\left(s_1^2/n_1\right)+\left(s_2^2/n_2\right)} \;,$$

where $\bar{X}$ = sample mean, s = sample standard deviation, and n = sample size, and for the "before" ($_1$) and "after" ($_2$) samples.

(McClave et al., 2005)

Appendix G: Solids Surface Analysis Before Orthophosphate Treatment

Figure 39. Digital Picture of Rm B14 Copper Pipe
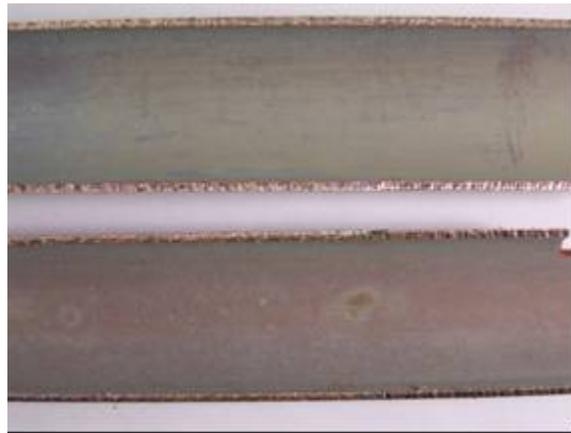
Figure 40. Digital Picture of Rm A6 Copper Pipe

Note thin film of deposits on majority of all pipes' interior surface.
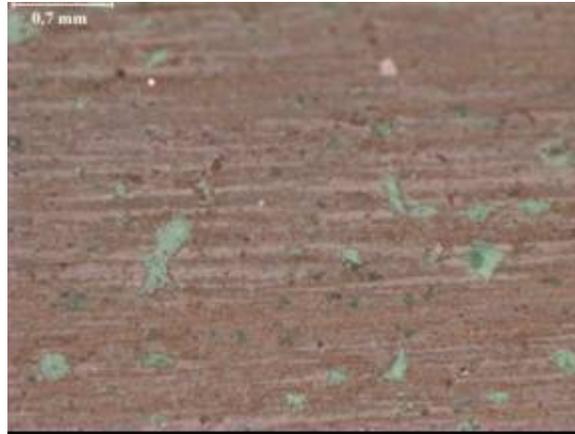
Figure 41. 3x Stereomicroscope Picture of Deposits on Pipe Wall
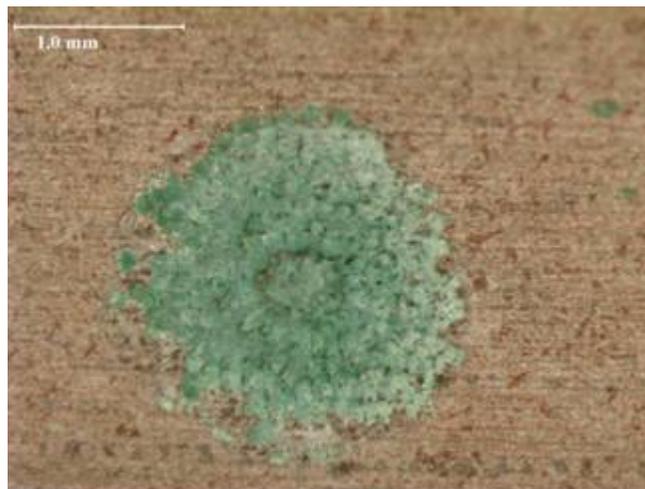

Figure 42. 3x Stereomicroscope Picture of Deposit on Pipe Interior
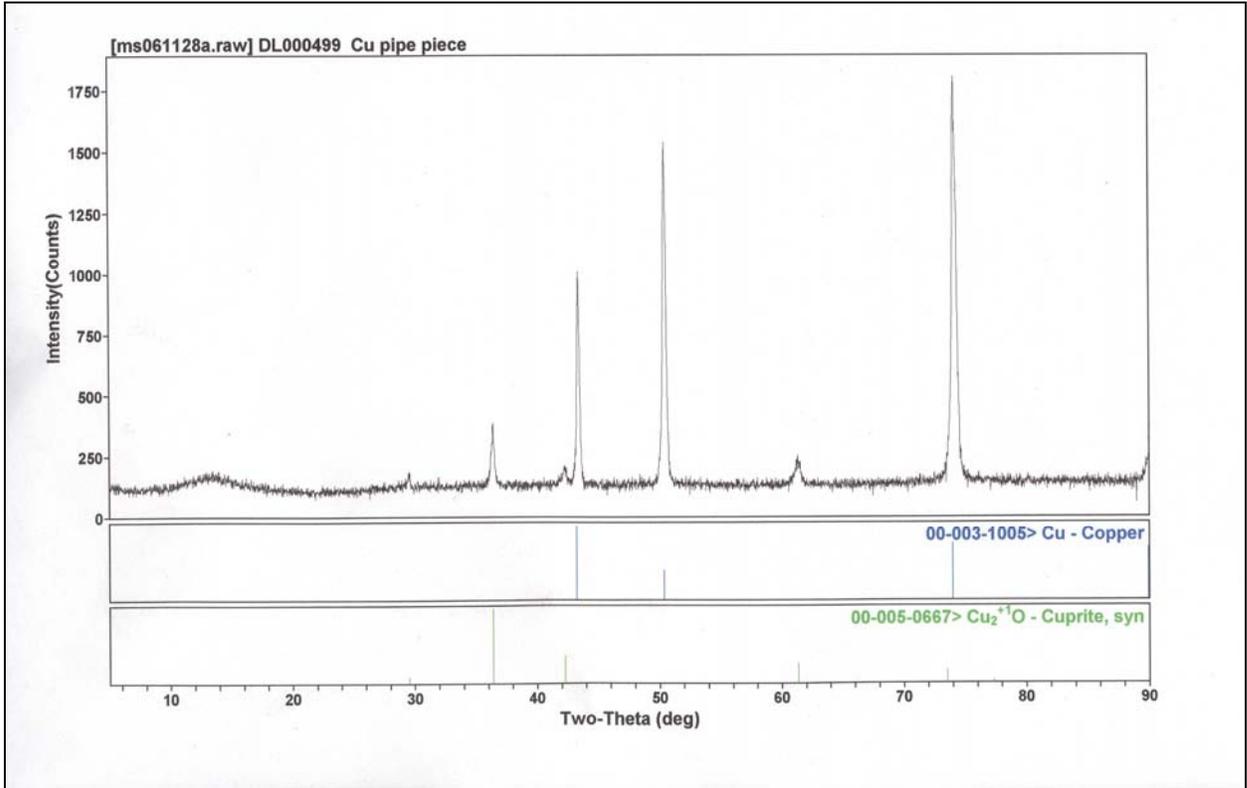
Figure 43. XRD Spectroscopic Analysis of Surface Solids

Note that XRD results suggest the presence of elemental copper metal and cuprite.

Table 9. Composition Analysis of Surface Solids (Pre-Treatment)

Spectrum	In stats.	C	O	Al	P	Cl	Ca	Fe	Cu	Total
Spectrum 1	Yes	10.45	10.16	0.13	1.74	0.77	0.19	0.29	76.27	100.00
Spectrum 2	Yes	10.02	9.95	0.15	1.67	0.80	0.23	0.30	76.87	100.00
Mean		10.24	10.06	0.14	1.70	0.79	0.21	0.30	76.57	100.00
Std. deviation		0.31	0.14	0.02	0.05	0.02	0.03	0.01	0.42	
Max.		10.45	10.16	0.15	1.74	0.80	0.23	0.30	76.87	
Min.		10.02	9.95	0.13	1.67	0.77	0.19	0.29	76.27	

All results in weight%

Appendix H: Solids Surface Analysis After Orthophosphate Treatment



Figure 44. Digital Pictures of Rm B14 Copper Pipe
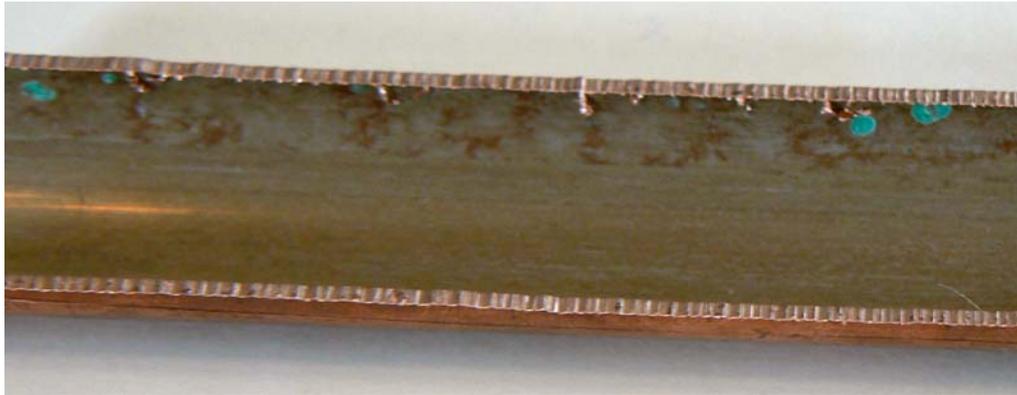
Figure 45. Digital Picture of Rm A6 Copper Pipe

Note copper deposits and thicker film on majority of all pipes' interior surface.
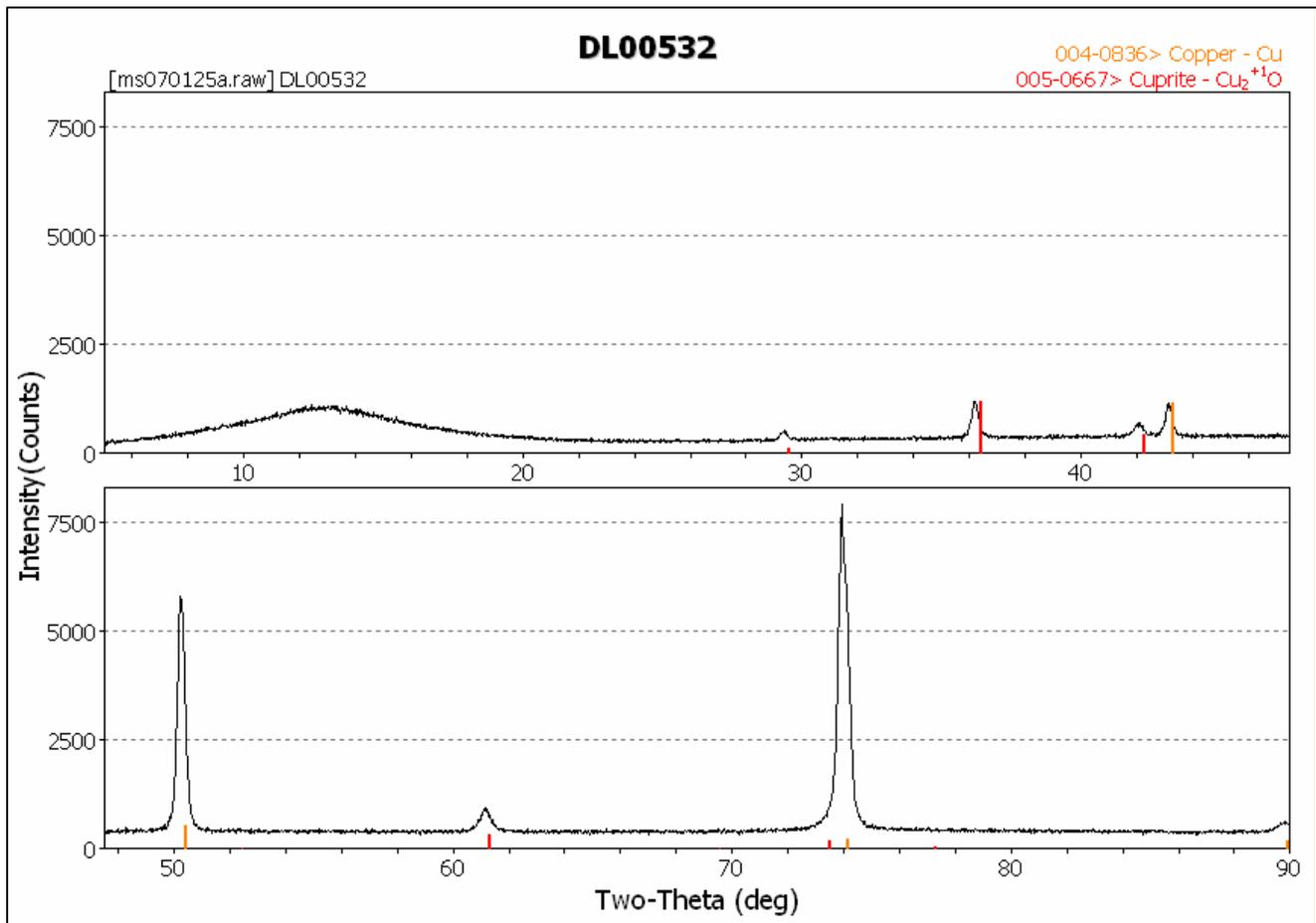
Figure 46. XRD Spectroscopic Analysis of Surface Solids

Note that XRD results suggest the presence of elemental copper metal and cuprite.

Table 10. Composition Analysis of Surface Solids (Post-Treatment)

Spectrum	In stats.	C	O	Al	Si	P	Cl	Ca	Fe	Cu	Total
Spectrum 1	Yes	17.03	12.64	0.14	0.16	1.98	0.28	0.32	0.55	66.90	100.00
Spectrum 2	Yes	21.06	12.95	-	-	1.89	0.20	0.28	0.56	63.05	100.00
Std. deviation		2.85	0.22	-	-	0.06	0.05	0.03	0.00	2.72	
Mean		19.05	12.80	0.14	0.16	1.94	0.24	0.30	0.56	64.97	
Max.		21.06	12.95	0.14	0.16	1.98	0.28	0.32	0.56	66.90	
Min.		17.03	12.64	0.14	0.16	1.89	0.20	0.28	0.55	63.05	

All results in weight%

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Vita

Major Stephen Grace graduated from Longmeadow High School in Longmeadow, Massachusetts. He entered undergraduate studies at the United States Air Force Academy, where he graduated with a Bachelor of Science degree in Civil Engineering and was commissioned in 1993.

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14. ABSTRACT

The purpose of this research was to investigate orthophosphate as a corrosion inhibitor for copper pipe in a high-alkalinity drinking water system. Specifically, this thesis sought to answer three research questions regarding the impact of orthophosphate treatment, the nature of the mechanism by which orthophosphate controls copper corrosion, and the value of equilibrium modeling in predicting orthophosphate's effects. The research questions were answered through a comprehensive literature review and experimental methodology integrating laboratory jar tests, water sampling and analysis from a field investigation, qualitative solids analysis, and equilibrium model application. This study analyzed field data obtained over the course of a year from a high alkalinity water system into which orthophosphate was added to control copper concentrations.

This field research generally supports results previously reported in the literature: in high alkalinity, neutral pH water, a dosage of 3 – 4 mg/L orthophosphate can reduce copper levels in a drinking water system from over 2 mg/L to below the 1.3 mg/L USEPA action level. While surface solid analysis did not provide conclusive evidence confirming the nature of orthophosphate's control mechanisms, jar tests and equilibrium solubility models were demonstrated to provide useful quantitative predictions of how orthophosphate reduces copper concentrations in various waters.

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